Thiazolinium Salts and their Reactions with Nucleophiles

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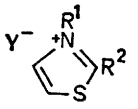
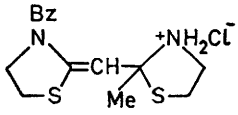
2,3-Dialkyl- and 3-alkyl-2-aryl-2-thiazolinium salts were prepared by quaternisation of the corresponding 2-thiazolines. Some 3-alkyl-2-alkylthio-2-thiazolinium salts were obtained by quaternisation of 2-alkylthio-2-thiazolines; the products included bicyclic salts obtained from αω-dibromides and 2-thiazoline-2-thiol. In some cases attempted quaternisation yielded only the 3-alkylthiazolidine-2-thiones, the original *S*-alkyl residue being lost. The behaviour of the salts with nucleophiles such as water, base, borohydride ion, and benzenethiolate ion was investigated. The oxidation of 2-thiazoline-2-thiol was also studied.

FOLLOWING a study of the reactions of nucleophiles with 3-alkylthiazolium salts (1),[1,2] and of how these were affected by the nature of substituents in the 2- and 3-positions, we have performed a similar investigation of 3-alkyl-2-thiazolinium salts (*e.g.* (2)].

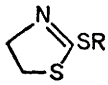


(1)

	R^1	R^2	Y
(2)	$PhCH_2$	Me	Br
(3)	$PhCH_2$	Ph	Br
(4)	Me	MeS	I
(5)	p-NO_2·C_6H_4·CH_2	p-NO_2·C_6H_4·CH_2·S	Br
(6)	$PhCH_2$	MeS	I
(7)	$PhCH_2$	$PhCH_2$·S	Br
(8)	$PhCH_2$	$PhCH_2$·S	Cl
(9)	Bz	$PhCH_2$·S	Br

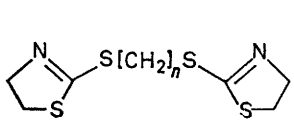


(10)

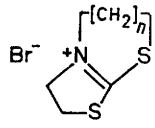


(11) R = H
(12) R = Me
(13) R = $PhCH_2$
(14) R = p-NO_2·C_6H_4·CH_2
(15) R = PhS
(16) R = Acyl

2-Alkyl- and 2-aryl-2-thiazolinium salts were obtained by the direct quaternisation of the corresponding 2-thiazolines with rigorous exclusion of moisture. With 2-methyl-2-thiazoline care had to be taken to avoid the formation of cyanine-type compounds, and the reaction of benzoyl chloride with 2-methyl-2-thiazoline yielded only the azomethine salt (10). We also desired to prepare 2-alkyl- and 2-acyl-thio-2-thiazolinium salts by *S*-alkylation or -acylation of 2-thiazoline-2-thiol (11) or its anion. 2-Methylthio-[3] and 2-benzylthio-[4] 2-thiazolines [(12) and (13), respectively] were known already, and simple alkylations giving other products proceeded smoothly; reactions with 1,2-dibromoethane and 1,3-dibromopropane, however, yielded not only the expected di(thiazoline)s [(17) and (18), respectively] but also the bicyclic salts [(19) and (20), respectively]. The di(thiazoline) (17) was converted into a dimethiodide, but this was unstable; other quaternisations could not be carried out.

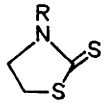


(17) $n = 2$
(18) $n = 3$



(19) $n = 2$
(20) $n = 3$

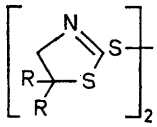
Acyl derivatives of 2-thiazoline-2-thiol (11) may be obtained by treatment with acyl halides but it appears not to have been established unequivocally whether these are in fact *S*-acyl derivatives[5,6] (2-acylthio-2-thiazolines) (16) or *N*-acyl derivatives[7-9] (3-acylthiazolidine-2-thiones), *e.g.* (21). The position of the C=O



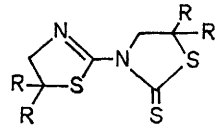
(21) R = Bz
(22) R = p-NO_2·C_6H_4·CO
(23) R = CO_2Et
(24) R = Me
(25) R = $PhCH_2$
(26) R = p-NO_2·C_6H_4·CH_2

band in their i.r. spectra does not permit unequivocal distinction between S·COR and N·COR, but the u.v. spectra of these compounds are unaffected by added acid, and they do not form picrates; these properties are similar to those of the corresponding *N*-alkyl compounds, *e.g.* (25), but contrast with those of the *S*-alkyl compounds, *e.g.* (13).

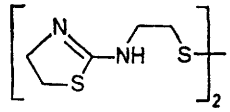
Attempts to make a 2-thiazolin-2-yl disulphide by oxidation of 2-thiazoline-2-thiol (11) with hydrogen peroxide were unsuccessful. Though 5,5-dimethyl-2-thiazoline-2-thiol is said to yield the disulphide[5] (28), in our hands 2-thiazoline-2-thiol (11), under similar conditions, yielded the thiazolinylthiazolidine-2-thione (29). However, the reported characterisation of compound (28)



(27) R = H
(28) R = Me



(29) R = H
(30) R = Me

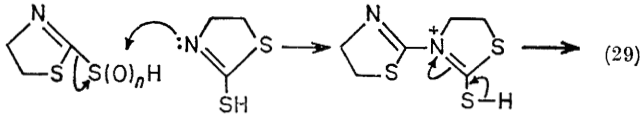


(31)

rests on a nitrogen analysis only, and this fits structure

[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] S. Gabriel, *Ber.*, 1889, **22**, 1152.
[4] J. C. Crawhall and D. F. Elliott, *J. Chem. Soc.*, 1952, 3094.
[5] J. B. Niederl and W. F. Hart, *J. Amer. Chem. Soc.*, 1939, **61**, 1145.
[6] A. H. Goddin and N. F. Searle, U.S.P. 2,516,313.
[7] L. B. Clapp and J. W. Watjen, *J. Amer. Chem. Soc.*, 1953, **75**, 1490.
[8] F. Runge, Z. El Heweki, H. J. Renner, and E. Taeger, *J. prakt. Chem.*, 1960, **11**, 284.
[9] C. S. Dewey and R. A. Bafford, *J. Org. Chem.*, 1965, **30**, 491.

(30) almost as well as it does (28). Compound (29) is probably formed by oxidation of the 2-thiol group of one molecule of the thiazoline (11), followed by nucleophilic attack by the nitrogen atom of a second molecule, with the oxygenated sulphur atom acting as a good leaving group (Scheme 1). However, compound (29) could also result from similar nucleophilic attack

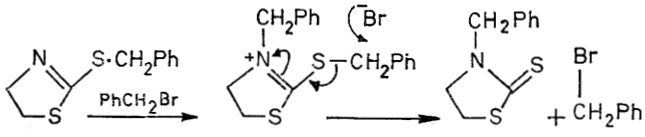


(29)

SCHEME 1

on a first-formed disulphide (27); an attempt to make the mixed disulphide (15) from benzenesulphenyl chloride and 2-thiazoline-2-thiol (11) in fact yielded compound (29). Oxidation of 2-thiazoline-2-thiol (11) with an excess of hydrogen peroxide gave the disulphide (31), which can also be obtained from hydrogen peroxide and compound (29).

Treatment of 2-methylthio-2-thiazoline (12) with methyl iodide and of 2-(*p*-nitrobenzyl)thio-2-thiazoline (14) with *p*-nitrobenzyl bromide, in both cases without solvent, yielded the expected *NS*-dialkyl salts [(4) and (5), respectively]; the latter salt is unstable. The former salt may also be obtained by *S*-methylation of 3-methylthiazolidine-2-thione [10] (24), and 3-benzyl-2-methylthio-2-thiazolinium iodide (6) may be obtained, though with greater difficulty, by methylation of 3-benzylthiazolidine-2-thione [11] (25); such thiones are resistant to attack by less powerful alkylating agents than methyl iodide, however. When heated with benzyl bromide, 2-benzylthio-2-thiazoline (13) gave 3-benzylthiazolidine-2-thione (25) instead of the expected *NS*-dibenzyl salt (7). This reaction proceeded more slowly in chloroform solution; t.l.c. under these conditions established that it went to completion, and that the thione (25) and benzyl bromide were the only products; the reaction also went to completion in the presence of only a catalytic quantity (0·1 mol.) of benzyl bromide. This could be explained by initial *N*-benzylation to yield an unstable *NS*-dibenzyl salt, followed by internal nucleophilic attack on the latter by halide ion to yield the thione (Scheme 2). This interpretation is supported by the fact that the *NS*-dialkyl salt (5) can be decomposed under similar conditions, to yield the thione (26), in essentially quantitative yield. The ease of breakdown of the intermediate *NS*-dialkyl salt would depend on the susceptibility towards nucleophilic attack of the carbon atom adjacent to sulphur in the 2-substituent, and also on the relative effectiveness of the halide ion as an internal nucleophile. Thus the *NS*-dimethyl salt (4) may be isolated and is apparently stable, whereas the *NS*-dibenzyl salt (7) could not be obtained. Attempts to make an *NS*-dibenzyl salt (8) containing a less effective internal nucleophile, by use of benzyl chloride in chloroform at 120°, were unsuccessful, no quaternisation taking place; under more vigorous conditions only the thione (25) and benzyl chloride could be obtained. Treatment of 2-benzylthio-2-thiazoline (13) with *p*-nitrobenzyl bromide and of 2-(*p*-nitrobenzyl)thio-2-thiazoline (14) with benzyl bromide in chloroform yielded, in each case, the expected mixture of thiones [(25) and (26)] and bromides in approximately equimolar proportions; this is unlikely to be an equilibrium situation, however, as the thiones, once formed, do not appear to undergo *S*-alkylation under the conditions of the reaction.

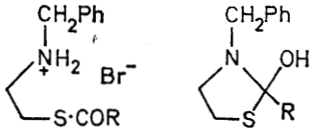


SCHEME 2

Treatment of 2-benzylthio-2-thiazoline (13) with benzoyl bromide in cold benzene yielded the unstable 3-benzoyl-2-benzylthio-2-thiazolinium bromide (9), which decomposed when heated to give the *N*-benzoylthione (21) and the hydrobromide of 2-benzylthio-2-thiazoline (13. The first product probably results from nucleophilic attack at the benzylic carbon atom, as in the case of the *N*-alkyl salt and, as before, benzyl bromide can be detected. The nature of the second product suggests formation is presumably formed by hydrolysis of the acyl bromide during work-up. That this latter breakdown of the original salt is not merely hydrolytic (atmospheric moisture) is shown by the fact that water actually converts it into a dithiocarbonate (see later).

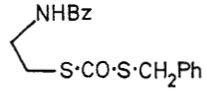
Action of Nucleophiles.—(a) *Water.* 3-Benzyl-2-methyl- and 3-benzyl-2-phenyl-2-thiazolinium bromide [(2) and (3), respectively] are partially hydrolysed in water to yield the *S*-acylthioalkylammonium salts (32) and (33), respectively. Equilibrium was attained at

$Me_2C(S{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2Ph)_2$ (36)



(32) R = Me
(33) R = Ph

(34) R = Me
(35) R = Ph



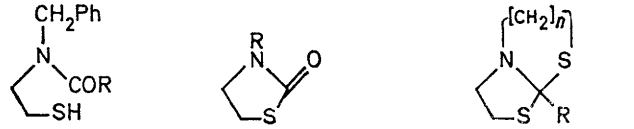
(37)

room temperature with the 2-methyl salt (2) (*cf.* 2-methyl-2-thiazoline itself [12]) after 48 hr.; the equilibrium mixture corresponded to *ca.* 65% *S*-acylthioalkylammonium salt (32) and *ca.* 35% thiazolinium salt (2); with the 2-phenyl salt (3) equilibration was more rapid, and the mixture contained a higher proportion of thiazolinium salt. Equilibrium could be attained *via* the pseudo-bases (34) and (35), respectively, but these could not be detected in either case. Adjustment of the pH of a solution in aqueous acetone (used to prevent deposition of the *S*-acylthioalkylammonium salt) of the 2-methylthiazolinium salt (2) to 7 led to loss of the

[10] J. W. Batty and B. C. L. Weedon, *J. Chem. Soc.*, 1949, 786.
[11] C. K. Bradsher, F. C. Brown, and E. F. Sinclair, *J. Amer. Chem. Soc.*, 1956, **78**, 6189.
[12] E. Felder and D. Pitré, *Gazzetta*, 1959, **89**, 1079.

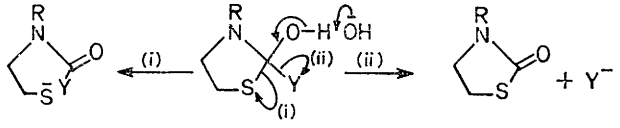
acetyl group and formation of the salt of the thioacetal (36). The action of water on 3-benzoyl-2-benzylthio-2-thiazolinium bromide (9) yielded the dithiocarbonate (37); this too could be produced *via* a pseudo-base.

(b) *Hydroxide ion.* 3-Benzyl-2-methyl- and 3-benzyl-2-phenyl-2-thiazolinium bromides [(2) and (3), respectively] underwent ring opening in the cold with base to yield the acylamino-thiols (38) and (39), respectively, characterised as their *S*-*p*-nitrobenzyl ethers. This ring fission, which could be reversed by treatment with



(38) R = Me (40) R = Me (44) R = H, n = 2
(39) R = Ph (41) R = p-NO_2·C_6H_4·CH_2 (45) R = H, n = 3
(42) R = $[CH_2]_2$·SH (46) R = PhS, n = 2
(43) R = $[CH_2]_3$·SH (47) R = PhS, n = 3

acid, could proceed *via* pseudo-bases [(34) and (35), respectively] to yield the acylamino-thiols directly [Scheme 3 (i)], but it was interesting that the *S*-acylthioalkylammonium salts (32) and (33), obtained from the action of water on the original thiazolinium salts (2) and (3) underwent base-catalysed rearrangement (*cf.* refs. 12 and 13) to give the acylamino-thiols (38) and (39). The action of base on *NS*-dialkylthiazolinium salts (4) and (5) yielded 3-alkylthiazolidine-2-ones (40) and (41), respectively. This decomposition could again proceed through a pseudo-base [Scheme 3 (ii)] the nature of the product then being dependent on the relative tendencies of the 2-thioalkyl group and the ring sulphur atom to act as leaving groups. This difference in behaviour, de-

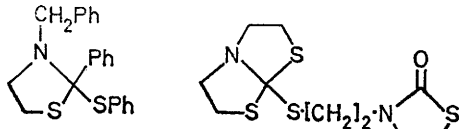


SCHEME 3

pending on the nature of the 2-substituent, resembles that encountered in the case of 2-substituted thiazolium salts (1).[2b] The bicyclic salts (19) and (20) behaved similarly, one ring being opened, and the resultant 3-mercaptoalkylthiazolidine-2-ones (42) and (43), respectively, were characterised as disulphides. In the case of the bicyclic salt (20) spectroscopic evidence (n.m.r. and i.r.) indicates that only the six-membered ring underwent fission.

(c) *Borohydride ion.* 3-Benzyl-2-methyl- and 3-benzyl-2-phenyl-2-thiazolinium bromides [(2) and (3), respectively] were reduced by sodium borohydride to yield the corresponding thiazolidines; the reduction was carried out in dimethyl formamide, since preferential base-catalysed ring-opening occurred in aqueous solution. The bicyclic salts (19) and (20) were reduced in anhydrous ethanol to yield the corresponding bicyclic thiazolidines (44) and (45), respectively. These reactions parallel the first stage in the reduction of thiazolium salts (1) to thiazolidines.[2c]

(d) *Benzenethiolate ion.* The bicyclic salts (19) and (20) reacted with sodium benzenethiolate in anhydrous ethanol to yield the adducts (46) and (47), respectively; a similar adduct (48) was obtained from 3-benzyl-2-phenylthiazolinium bromide (3). These reactions are exceedingly susceptible to traces of moisture, which cause base-catalysed ring-opening. In one case, with the bicyclic salt (19) in methanol, the adduct (49) was obtained from attack of partly ring-opened material (42) on unchanged bicyclic salt. The adduct (46) was de-



(48) (49)

composed to the original bicyclic salt (19) on addition of acid.

EXPERIMENTAL

M.p.s were obtained with a Gallenkamp electrothermal apparatus or a Kofler hot-stage. U.v. spectra were measured for solutions in 95% aqueous ethanol; i.r. spectra were obtained with a Perkin-Elmer 257 or a Unicam SP 200 instrument; n.m.r. spectra were obtained with a Perkin-Elmer R10 (60 MHz) or a Varian HA 100 instrument, tetramethylsilane being used as internal standard except for solutions in deuterium oxide, for which t-butyl alcohol (τ 8·78) was employed. T.l.c. was performed on silica gel GF 254 plates, with 1 : 1 benzene–methylene dichloride as the usual solvent mixture.

3-*Benzyl*-2-*methyl*-2-*thiazolinium Bromide* (2).—2-Methyl-2-thiazoline (10·1 g., 1 mol.) and benzyl bromide (17·1 g., 1 mol.) were dissolved in dry acetonitrile and left for 16 hr. at room temperature. The orange crystals (24 g.) formed yielded the *thiazolinium bromide* (17 g., 63%), m.p. 240—242° [from acetonitrile (charcoal)] (Found: C, 48·2; H, 5·1; N, 5·4. $C_{11}H_{14}BrNS$ requires C, 48·5; H, 5·2; N, 5·2%), $\nu_{max.}$ (Nujol) 1600 cm^{-1} (C=$\overset{+}{N}$), τ (D_2O) 7·3 (3H, s, Me), 6·4 (2H, t, J 8·0 Hz, CH_2·S), 5·6 (2H, t, J 8·0 Hz, CH_2·$\overset{+}{N}$), 5·0 (2H, s, PhCH_2), and 2·5 (5H, s, Ph).

3-*Benzyl*-2-*phenyl*-2-*thiazolinium Bromide* (3).—Redistilled 2-phenyl-2-thiazoline [14] (11·3 g., 1 mol.) and benzyl bromide (11·8 g., 1 mol.) were refluxed in dry acetonitrile for 4 hr. The solid that separated on cooling and scratching gave the *thiazolinium bromide* (10 g., 45%), m.p. 125—127° (from dry acetonitrile) (Found: C, 57·2; H, 4·8; N, 3·9. $C_{16}H_{16}$BrNS requires C, 57·5; H, 4·8; N, 4·2%), $\nu_{max.}$ (Nujol) 1605 cm.$^{-1}$ (C=$\overset{+}{N}$), τ (D_2O) 6·3 (2H, t, J 8·0 Hz, CH_2·S), 5·5 (2H, t, J 8·0 Hz, CH_2·$\overset{+}{N}$), 5·1 (2H, s, PhCH_2), and 2·0—2·7 (10H, 2 × Ph).

3-*Methyl*-2-*phenyl*-2-*thiazolinium Iodide*.—2-Phenyl-2-thiazoline (1·25 g.), dissolved in methyl iodide (5 ml.), was left for 16 hr. at room temperature. The crystals formed yielded the *thiazolinium iodide* (0·3 g., 12%), m.p. 168—

[13] J. Baddiley and E. M. Thain, *J. Chem. Soc.*, 1951, 3425.
[14] S. Gabriel and C. von Hirsch, *Ber.*, 1896, **29**, 2609.

169° (from dry acetonitrile) (Found: C, 39·3; H, 4·0; N, 4·4. $C_{10}H_{12}INS$ requires C, 39·4; H, 4·0; N, 4·6%), $\nu_{max.}$ (Nujol) 1630 cm.$^{-1}$ (C=$\overset{+}{N}$), τ (D_2O) 6·5 (3H, s, Me), 6·2 (2H, t, CH_2·S), 5·3 (2H, t, CH_2·$\overset{+}{N}$), and 2·0—2·3 (5H, Ph).

Reaction of 2-Methyl-2-thiazoline with Benzoyl Chloride.—Benzoyl chloride (1·4 g., 1 mol.) was added slowly to 2-methyl-2-thiazoline (1·0 g., 1 mol.) cooled to 5°; a deep red colouration developed and colourless crystals separated. Recrystallisation from ethanol yielded 2-(3-*benzoylthiazolidin*-2-*ylidenemethyl*)-2-*methylthiazolidinium chloride* (10), m.p. 203—204° (Found: C, 52·5; H, 5·7; N, 8·8. $C_{15}H_{19}ClN_2OS_2$ requires C, 52·5; H, 5·6; N, 8·2%), τ ($CDCl_3$) 7·6 (3H, s, Me), 6·8 (2H, t, CH_2·S), 6·4 (4H, m, 2 × CH_2), 5·8 (2H, t, CH_2·$\overset{+}{N}$), 2·4 (1H, s, =CH), and 2·0—2·6 (5H, Ph).

2-(p-*Nitrobenzylthio*)-2-*thiazoline* (14).—2-Thiazoline-2-thiol (11·9 g., 1 mol.) was dissolved in a solution of sodium ethoxide [from sodium (2·3 g., 1 mol.) in dry ethanol (900 ml.)], and *p*-nitrobenzyl bromide (21·6 g., 1 mol.) was slowly added. The red solution was set aside for 1 hr. at room temperature, then evaporated, and the residue was extracted with ether to yield (from ethanol) the *product* (20 g., 78%), m.p. 80—81° (Found: C, 47·3; H, 4·1; N, 11·0. $C_{10}H_{10}N_2O_2S_2$ requires C, 47·2; H, 4·0; N, 11·0%), τ ($CDCl_3$) 6·6 (2H, t, *J* 8·0 Hz, CH_2·S), 5·75 (2H, t, *J* 8·0 Hz, CH_2·$\overset{+}{N}$), 5·6 (2H, s, ArCH_2), and 1·8—2·5 (4H, C_6H_4), $\lambda_{max.}$ 218 and 270 nm. (ε 15,100 and 11,100), $\lambda_{max.}$ (H^+) 266 nm. (ε 20,600).

A similar procedure yielded 2-benzylthio-2-thiazoline (13) (67%), m.p. 45—47° (lit.,[4] 47°), $\lambda_{max.}$ 220 nm. (ε 17,600), $\lambda_{max.}$ (H^+) 259 nm. (ε 13,000). Its *hydrobromide* was also prepared, m.p. 173—174° (from ethanol) (Found: C, 41·2; H, 4·1; N, 4·8. $C_{10}H_{12}BrNS_2$ requires C, 41·4; H, 4·2; N, 4·8%).

Reaction of 1,2-Dibromoethane with 2-Thiazoline-2-thiol.—A solution of sodium 2-thiazoline-2-thiolate (28·5 g., 1 mol.) in acetone (150 ml.) was added (10 min.) to a cooled solution of 1,2-dibromoethane (37·6 g., 1 mol.) in acetone (50 ml.) with stirring. Sodium bromide (23 g.) was collected after 15 min. Colourless crystals (20 g.) which separated overnight yielded 2,3,5,6-*tetrahydrothiazolo*[2,3-b]*thiazolium bromide* (19) (13 g., 30%), m.p. 168—170° (from acetonitrile), $\nu_{max.}$ (Nujol) 1570 cm.$^{-1}$ (C=$\overset{+}{N}$), τ (D_2O) 5·8 (8H, s, 2 × CH_2·CH_2); *picrate*, m.p. 155—156° (Found: C, 35·5; H, 2·8; N, 15·3. $C_{11}H_{10}N_4O_7S_2$ requires C, 35·3; H, 2·7; N, 15·0%).

Evaporation of the acetonitrile mother liquors yielded 2,2′-(*ethylenedithio*)*di*-2-*thiazoline* (17) (3 g.), m.p. 127—128° (from ethanol) (Found: C, 36·2; H, 4·7; N, 10·7. $C_8H_{12}N_2S_4$ requires C, 36·3; H, 4·6; N, 10·6%); *dipicrate*, m.p. 153—155° (Found: C, 33·3; H, 2·7; N, 15·4. $C_{20}H_{18}N_8O_{14}S_4$ requires C, 33·2; H, 2·5; N, 15·5%); *dihydrobromide*, m.p. 230—232° (from ethanol) (Found: C, 22·3; H, 3·4; N, 6·5. $C_8H_{14}Br_2N_2S_4$ requires C, 22·5; H, 3·3; N, 6·6%), τ (CF_3·CO_2H) 6·0 (4H, s, CH_2·CH_2), 6·0 (4H, t, *J* 8·0 Hz, 2 × CH_2·S), and 5·3 (4H, t, *J* 8·0 Hz, 2 × CH_2·$\overset{+}{N}$).

The yield of the dithiazoline was increased (60%) by using 2 mol. of sodium 2-thiazoline-2-thiolate and adding the 1,2-dibromoethane solution to it.

Reaction of 1,3-Dibromopropane with 2-Thiazoline-2-thiol.—To a solution of sodium 2-thiazoline-2-thiolate (21·4 g., 1 mol.) in dry ethanol (150 ml.), 1,3-dibromopropane (36·5 g., 1 mol) was added with stirring during 15 min. Sodium bromide (14 g.) was collected after 15 min. Colourless crystals separated overnight (15 g.). The mother liquors were evaporated and the crystals and residue were extracted with ether. Recrystallisation from ethanol of the material insoluble in ether yielded 2,3,6,7-*tetrahydro*-5H-*thiazolo*-[2,3-b][1,3]*thiazinium bromide* (20) (18 g., 45%), m.p. 267—270° (Found: C, 29·7; H, 4·1; N, 6·1. $C_6H_{10}BrNS_2$ requires C, 30·0; H, 4·2; N, 5·8%), $\nu_{max.}$ (Nujol) 1590 cm.$^{-1}$ (C=$\overset{+}{N}$), τ (D_2O) 7·6 (2H, quintet, C·CH_2·C), 6·6 (2H, t, C·CH_2·S), 6·1—6·3 (4H, C·CH_2·$\overset{+}{N}$ and CH_2·S), and 5·5 (2H, t, CH_2·$\overset{+}{N}$); *picrate*, m.p. 141—142° (from ethanol) (Found: C, 37·3; H, 3·4; N, 14·5. $C_{12}H_{12}N_4O_7S_2$ requires C, 37·1; H, 3·1; N, 14·4%).

The ethereal extract was extracted with dilute hydrobromic acid; the aqueous acid extract was neutralised with sodium carbonate, and the mixture was extracted with ether. The dried ($MgSO_4$) ether extract was evaporated to yield 2,2′-(*trimethylenedithio*)*di*-2-*thiazoline* (18) as an uncrystallisable gum, τ ($CDCl_3$) 7·8 (2H, quintet, C·CH_2·C), 6·8 (4H, t, CH_2·C·CH_2), 6·6 (4H, t, *J* 7·0 Hz, 2 × CH_2·S), and 5·8 (4H, t, *J* 7·0 Hz, 2 × CH_2·$\overset{+}{N}$); *picrate*, m.p. 136—138° (from ethanol) (Found: C, 34·0; H, 2·8; N, 15·1. $C_{21}H_{20}N_8O_{14}S_4$ requires C, 34·2; H, 2·7; N, 15·2%).

Ethyl 2-Thioxothiazolidine-3-carboxylate (23).—Sodium 2-thiazoline-2-thiolate (14·1 g., 1 mol.) was dissolved in dry ethanol (250 ml.) and ethyl chloroformate (10·8 g., 1 mol.) was added. Sodium chloride separated; after 15 min. the solvent was removed and the residue was extracted with chloroform. The dried ($MgSO_4$) extract was evaporated to yield the *ester* (24 g., 95%) as a yellow oil. A portion was purified (molecular still) (Found: C, 37·9; H, 4·9; N, 7·6. $C_6H_9NO_2S_2$ requires C, 37·7; H, 4·7; N, 7·3%), $\nu_{max.}$ 1750 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 8·7 (3H, t, *J* 6·0 Hz, CH_2·CH_3), 6·0 (2H, t, *J* 7·0 Hz, CH_2·S), 5·8 (2H, q, *J* 6·0 Hz, O·CH_2·Me), and 5·6 (2H, t, *J* 7·0 Hz, CH_2·N), $\lambda_{max.}$ 262 and 299 nm. (ε 12,900 and 10,200), $\lambda_{max.}$ (H^+) 261 and 299 nm. (ε 13,700 and 10,900).

Similar procedures yielded 3-benzoylthiazolidine-2-thione (21),[8] $\lambda_{max.}$ 245 and 280 nm. (ε 9580 and 15,400), $\lambda_{max.}$ (H^+) 247 and 280 nm. (ε 9340 and 15,060), and 3-(*p*-nitrobenzoyl)-thiazolidine-2-thione (22),[7-9] $\lambda_{max.}$ 260 and 280 nm. (ε 13,000 and 15,000), $\lambda_{max.}$ (H^+) 262 and 281 nm. (ε 12,900 and 14,670).

3-*Phenylcarbamoylthiazolidine*-2-*thione*.—2-Thiazoline-2-thiol (1·19 g., 1 mol.) was warmed with phenyl isocyanate (1·19 g., 1 mol.) until the melt became homogeneous. On cooling, the melt solidified and yielded the *substituted urea* (1·0 g., 40%), m.p. 168—169° (from ethanol) (Found: C, 50·2; H, 4·4; N, 11·7. $C_{10}H_{10}N_2OS_2$ requires C, 50·4; H, 4·2; N, 11·8%), $\nu_{max.}$ (Nujol) 1700 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 6·8 (2H, t, *J* 8·0 Hz, CH_2·S), 5·3 (2H, t, *J* 8·0 Hz, CH_2·N), 2·4—2·8 (5H, Ph), $\lambda_{max.}$ 234 and 277 nm. (ε 15,400 and 15,100), $\lambda_{max.}$ (H^+) 235 and 276 nm. (ε 21,400 and 14,800).

None of these *N*-acylthiazolidine-2-thiones formed picrates.

Oxidation of 2-Thiazoline-2-thiol.—2-Thiazoline-2-thiol (11·9 g., 1 mol.) was dissolved in acetone (150 ml.) and aqueous hydrogen peroxide (3%; 150 ml.) was slowly added. Heat was evolved and the flask was cooled. A yellow oil separated and was extracted into chloroform; the acetone solution was evaporated and the aqueous residue was extracted with chloroform. The combined,

dried ($MgSO_4$), extracts were evaporated to yield a yellow gum (8 g.) which we could not crystallise. The gum was extracted with dilute hydrochloric acid, and the acidic extract was then neutralised with aqueous sodium hydroxide. The separated oil was extracted into chloroform, the extract was dried ($MgSO_4$) and evaporated, and the residue yielded 3-(2-*thiazolin*-2-*yl*)*thiazolidine*-2-*thione* (29) (4 g., 40%), m.p. 78—80° (from ethanol) (Found: C, 35·3; H, 4·0; N, 14·0; S, 47·1%; M^+, 203·9823. $C_6H_8N_2S_3$ requires C, 35·3; H, 3·9; N, 13·7; S, 47·1%; *M*, 203·9850), $\nu_{max.}$ (Nujol) 1580 (C=N) and 1030 $cm.^{-1}$ (C=S), τ ($CF_3{\cdot}CO_2H$) 6·3 (2H, t, $CH_2{\cdot}S{\cdot}C{=}S$), 6·2 (2H, t, $CH_2{\cdot}S$), 5·6 (2H, t, $CH_2{\cdot}N{\cdot}C{=}S$), and 5·2 (2H, t, $CH_2{\cdot}N$); *picrate*, m.p. 152—154° (from ethanol) (Found: C, 33·8; H, 2·5; N, 16·3. $C_{12}H_{11}N_5O_7S_3$ requires C, 33·2; H, 2·6; N, 16·2%); *hydrochloride*, m.p. 198—200° (from butan-1-ol) (Found: C, 30·1; H, 3·9; N, 11·5; S, 39·9. $C_6H_9ClN_2S_3$ requires C, 29·9; H, 3·8; N, 11·6; S, 39·9%). Oxidation in hydrochloric acid solution yielded the hydrochloride directly (75%).

Oxidation until no more hydrogen peroxide was used up (24 hr.) yielded a solution which on basification deposited a sticky solid. This yielded *bis*-[2-(2-*thiazolin*-2-*ylamino*)-*ethyl*] *disulphide* (31) (55%), m.p. 140—142°, τ ($CDCl_3$) 7·1 (2H, t, *J* 6·0 Hz, $CH_2{\cdot}S{\cdot}S$), 6·7 (2H, t, *J* 7·0 Hz, $CH_2{\cdot}N$), and 5·1 (1H, t, NH, exchangeable); *dipicrate*, m.p. 232—233° (from ethanol) (Found: C, 33·7; H, 3·4; N, 17·6. $C_{22}H_{24}N_{10}O_{14}S_4$ requires C, 33·8; H, 3·1; N, 17·9%); *dihydrochloride*, m.p. 195—198° (from ethanol) (Found: C, 30·3; H, 5·3; N, 14·0. $C_{10}H_{20}Cl_2N_4S_4$ requires C, 30·4; H, 5·1; N, 14·2%).

3-*Benzylthiazolidine*-2-*thione* (25) was unaffected by hydrogen peroxide in aqueous acetone solution at room temperature.

Reaction of Benzenesulphenyl Chloride with 2-*Thiazoline*-2-*thiol*.—To benzenesulphenyl chloride [15] (3 g.), in dry acetone (10 ml.) was added a solution of sodium 2-thiazoline-2-thiolate (1 mol.) in acetone. A vigorous reaction took place but no crystalline products were isolated. Treatment with ethanolic picric acid, however, yielded the picrate of 3-(2-thiazolin-2-yl)thiazolidine-2-thione (29), m.p. and mixed m.p. 152—154°.

Treatment of the sodium 2-thiazoline-2-thiolate with sodium benzylthiolsulphonate [16] also failed to yield a mixed disulphide.

3-(p-*Nitrobenzyl*)-2-(p-*nitrobenzylthio*)-2-*thiazolinium Bromide* (5).—2-(p-Nitrobenzylthio)-2-thiazoline (2·45 g., 1 mol.) and *p*-nitrobenzyl bromide (2·16 g., 1 mol.) were heated together at 90° (4 hr.), then cooled and triturated twice with acetone to yield the NS-*dialkyl bromide* (4·5 g., 95%), m.p. 138—139° (Found: C, 43·1; H, 3·7; N, 9·2. $C_{17}H_{16}BrN_3O_4S_2$ requires C, 43·4; H, 3·4; N, 8·9%). Reaction at a higher temperature results in less salt being formed, and heating the solid salt above 90° for a few minutes gives 3-(*p*-nitrobenzyl)thiazolidine-2-thione (26) (see later).

2-Methylthio-2-thiazoline, when set aside overnight with methyl iodide at room temperature, yielded 3-methyl-2-methylthio-2-thiazolinium iodide (4), m.p. 138—139° (from ethanol) (lit.,[10] 132°), τ (D_2O) 7·0 (3H, s, MeS), 6·5 (3H, s, MeN^+), 6·2 (2H, t, $CH_2{\cdot}S$), and 5·5 (2H, t, $CH_2{\cdot}N^+$).

3-*Benzyl*-2-*methylthio*-2-*thiazolinum Iodide* (6).—3-Benzylthiazolidine thione [11] (0·73 g.) was heated with methyl iodide (30 ml.) in a sealed tube at 80° (24 hr.). The methyl iodide was then evaporated off and a solution of the residue in chloroform was washed with aqueous sodium thiosulphate solution to remove iodine. The solution was then dried ($MgSO_4$) and evaporated to dryness, and the residue gave the NS-*dialkyl iodide* (0·4 g., 33%), m.p. 110—111° [from ethanol–ethyl acetate (1 : 1)] (Found: C, 37·6; H, 4·2; N, 4·2. $C_{11}H_{14}INS_2$ requires C, 37·6; H, 4·0; N, 4·0%), τ ($CDCl_3$) 7·0 (3H, s, Me), 5·9 (2H, t, *J* 8·0 Hz, $CH_2{\cdot}S$), 5·3 (2H, t, *J* 8·0 Hz, $CH_2{\cdot}N^+$), 4·9 (2H, s, $PhCH_2$), and 2·5 (5H, s, Ph).

2,2′-(*Ethylenedithio*)*di*-2-*thiazoline Dimethiodide*.—2,2′-(Ethylenedithio)di-2-thiazoline (17) (3·66 g., 1 mol.) and methyl iodide (8·0 g., 2 mol.) in dry acetone (150 ml.) were refluxed together for 8 hr. Yellow crystals separated which, after trituration with chloroform, yielded the *dimethiodide* (2·75 g., 50%), m.p. 146—148° (Found: C, 22·1; H, 3·2; N, 5·3. $C_{10}H_{18}I_2N_2S_4$ requires C, 21·9; H, 3·3; N, 5·1%), τ ($CF_3{\cdot}CO_2H$) 6·4 (6H, s, 2 × Me), 6·0 (8H, 4 × $CH_2{\cdot}S$), and 5·3 (4H, t, 2 × $CH_2{\cdot}N^+$).

Recrystallisation of this salt from ethanol resulted in isomerisation to give a product, m.p. 180—182° (Found: C, 21·8; H, 3·3; N, 4·9. Calc. for $C_{10}H_{18}I_2N_2S_4$: C, 21·9; H, 3·3; N, 5·1%), τ ($CF_3{\cdot}CO_2H$) 7·0—6·8 (8H, m, 2 × $CH_2{\cdot}CH_2$), 6·5 (3H, s, Me), 6·2 (3H, s, Me), 5·47 (2H, t, *J* 7·0 Hz, $CH_2{\cdot}S$), and 5·35 (2H, t, *J* 7·0 Hz, $CH_2{\cdot}N^+$).

Reaction of 2-*Benzylthio*-2-*thiazoline with Benzyl Bromide*.—2-Benzylthio-2-thiazoline (1·05 g., 1 mol.) and benzyl bromide (0·85 g., 1 mol.) were heated together at 100° for 1 hr.; t.l.c. then showed none of the original thiazoline to be present. The melt solidified when cool and yielded 3-benzylthiazolidine-2-thione (25) (0·7 g., 65%), m.p. 131—133° (from ethanol) (lit.,[11] 132—133°) (Found: C, 57·1; H, 5·6; N, 6·7. Calc. for $C_{10}H_{11}NS_2$: C, 57·4; H, 5·3; N, 6·7%), τ ($CDCl_3$) 6·8 (2H, t, *J* 8·0 Hz, $CH_2{\cdot}S$), 6·05 (2H, t, *J* 8·0 Hz, $CH_2{\cdot}N$), 5·05 (2H, s, $PhCH_2$), and 2·7 (5H, s, Ph), $\lambda_{max.}$ 276 nm. (ε 15,800), $\lambda_{max.}$ (H^+) 276 nm. (ε 15,200).

When the reaction was repeated with a catalytic quantity only of benzyl bromide (0·1 mol.), t.l.c. showed complete conversion of the original 2-alkylthio-2-thiazoline to the thione in 2 hr.

Reaction of 2-*Benzylthio*-2-*thiazoline and* p-*Nitrobenzyl Bromide*.—Similar treatment of 2-benzylthio-2-thiazoline with *p*-nitrobenzyl bromide yielded 3-(p-*nitrobenzyl*)*thiazolidine*-2-*thione* (26) (40%), m.p. 150—152° (from ethanol) (Found: C, 47·3; H, 4·3; N, 10·9. $C_{10}H_{10}N_2O_2S_2$ requires C, 47·2; H, 4·0; N, 11·0%), τ ($CDCl_3$) 6·7 (2H, t, $CH_2{\cdot}S$), 6·0 (2H, t, $CH_2{\cdot}N$), 4·9 (2H, s, $ArCH_2$), and 1·8—2·5 (4H, C_6H_4), $\lambda_{max.}$ 271 nm. (ε 22,000), $\lambda_{max.}$ (H^+) 272 nm. (ε 24,000).

Treatment of 2-alkylthio-2-thiazolines with alkyl halides in dry chloroform under reflux led to a slower reaction that could be followed by t.l.c. and that required up to 48 hr. for completion. Use of a halide with an alkyl group different from that of the 2-alkylthio-2-thiazoline yielded both thiones and both halides. Thus with 2-benzylthio-2-thiazoline and *p*-nitrobenzyl bromide the products were 3-(*p*-nitrobenzyl)- and 3-benzyl-thiazolidine-2-thione [(26) and (25), respectively] and benzyl and *p*-nitrobenzyl bromides. Preparative t.l.c., elution of the bands with ethanol, and comparison of the u.v. spectra of the solutions established that the two thiones were present in approximately equimolar proportions.

[15] H. Lecher, F. Holschneider, K. Koberle, W. Speer, and P. Stocklin, *Ber.*, 1925, **58**, 409.
[16] A. Purgotti, *Gazzetta*, 1890, **20**, 24.

Reaction of 2-Benzylthio-2-thiazoline with Benzyl Chloride.—No reaction occurred in boiling chloroform, or in chloroform at 120° (72 hr.); at 100° (no solvent; 24 hr.) 3-benzylthiazolidine-2-thione and benzyl chloride were formed.

Reaction of 2-(p-Nitrobenzylthio)-2-thiazoline with Methyl Iodide.—2-(*p*-Nitrobenzylthio)-2-thiazoline (0·82 g.) and methyl iodide (10 ml.) were heated in a sealed tube at 100° for 24 hr. The solvent was then evaporated off and a solution of the residue in chloroform was extracted with aqueous sodium thiosulphate solution to remove iodine. The chloroform layer was dried ($MgSO_4$) and evaporated to yield yellow crystals of 4-nitrobenzyl iodide, m.p. 127—128° (from ethanol) (lit.,[17] 127°). The sodium thiosulphate washings deposited crystals of 3-methyl-2-methylthio-2-thiazolinium iodide, m.p. and mixed m.p. 135—136° (lit.,[10] 132°).

3-Benzoyl-2-benzylthio-2-thiazolinium Bromide (9).—2-Benzylyhio-2-thiazoline (2·1 g., 1 mol.) was dissolved in dry benzene (10 ml.) and redistilled benzoyl bromide (1·85 g., 1 mol.) was added dropwise. A solid began to separate at once and the mixture ultimately all but solidified. The solid was filtered off and washed with dry benzene, and the residual benzene was removed over paraffin wax in a vacuum desiccator to yield *3-benzoyl-2-benzylthio-2-thiazolinium bromide* (3·5 g., 87%), m.p. 100° (decomp.) (Found: C, 51·1; H, 4·1; N, 3·4. $C_{17}H_{16}BrNOS_2$ requires C, 51·8; H, 4·1; N, 3·6%), $\nu_{max.}$ 1700 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 6·6 (2H, t, *J* 6·0 Hz, CH_2·S), 6·3 (2H, t, *J* 6·0 Hz, CH_2·$\overset{+}{N}$), 5·8 (2H, s, PhCH_2), and 2·6—2·7 (10H, 2 × Ph).

Action of Heat on 3-Benzoyl-2-benzylthio-2-thiazolinium Bromide.—The salt (0·5 g.) was heated at 110° for 15 min. A reduction in volume occurred and a yellow solid was produced. The odour of benzoyl bromide was detected and t.l.c. showed the presence of 3-benzoylthiazolidine-2-thione (21), 2-benzylthio-2-thiazoline (13) hydrobromide, benzyl bromide, and benzoyl bromide. On trituration with ethanol colourless crystals of 2-benzylthio-2-thiazoline hydrobromide were obtained, m.p. and mixed m.p. 173—174°.

Action of Nucleophiles.—(a) *Water.* (i) *3-Benzyl-2-Methyl-2-thiazolinium bromide* (2). 3-Benzyl-2-methyl-2-thiazolinium bromide (1 g.) in water (5 ml.) was refluxed for 30 min. (or left overnight at room temperature). Evaporation then left a gum which yielded *2-acetylthioethyl(benzyl)ammonium bromide* (32) (0·6 g., 55%), m.p. 156—157° (from isobutyl alcohol) (Found: C, 45·6; H, 5·3; N, 4·7. $C_{11}H_{16}BrNOS$ requires C, 45·4; H, 5·6; N, 4·8%), $\nu_{max.}$ (Nujol) 2780, 2740, and 2410 (NH_2^+), and 1700 cm.$^{-1}$ (C=O), τ (D_2O) 7·6 (3H, s, Ac), 6·7 (4H, m, CH_2·CH_2·S), 5·7 (2H, s, PhCH_2), and 2·4 (5H, s, Ph).

Repetition (30 min. under reflux) in aqueous acetone solution with the pH adjusted from 3 to 7 (sodium hydrogen carbonate) led, after removal of solvent, to a gum, which yielded *2,2-bis-(2-benzylaminoethylthio)propane dihydrobromide* (36) (0·3 g., 30%), m.p. 193—194° (from isobutyl alcohol) (Found: C, 47·3; H, 6·2; N, 4·9. $C_{21}H_{32}Br_2N_2S_2$ requires C, 47·0; H, 6·0; N, 5·2%), $\nu_{max.}$ (Nujol) 2800, 2740, 2510, and 2390 ($\overset{+}{N}H_2$), and 1385 and 1365 cm.$^{-1}$ (CMe_2), τ (CF_3·CO_2H) 7·6 (6H, s, 2 × Me), 6·9 (4H, t, 2 × CH_2·S), 6·5 (4H, t, 2 × CH_2·N), 5·5 (4H, t, 2 × PhCH_2, becomes singlet on addition of D_2O), and 2·4 (10H, s, 2 × Ph).

The rate of ring opening of the salt (2) in deuterium oxide at 34° was studied by n.m.r. spectroscopy; no further change was found to take place after 48 hr. The relative proportions of unchanged salt (2) and ring-opened material (32) were determined by measuring the areas of the PhCH_2 peaks in the n.m.r. spectrum, and also those of the $C=\overset{+}{N}$ and C=O peaks in the i.r. spectrum: the ratio was found to be *ca.* 1 : 2.

2-Acetylthioethyl(benzyl)ammonium chloride was prepared as follows for comparison. 2-Benzylaminoethanethiol[18] (3·5 g.) was suspended in acetyl chloride (5 ml.) and stirred (*cf.* ref. 19). More acetyl chloride (5 ml.) was added later with stirring, and the excess was then removed by warming. The resultant solid was percolated with dry ether, and the residue was then washed and centrifuged with dry ether (× 3). The solid was dissolved in dimethylformamide (50 ml.) and concentrated hydrochloric acid (5 drops) was added, followed by dry ether (10 ml.) to induce crystallisation. *2-Acetylthioethyl(benzyl)ammonium chloride* (3 g., 67%), m.p. 155—157° (from isobutyl alcohol) had i.r. and n.m.r. spectra essentially identical with those of the corresponding hydrobromide.

(ii) *3-Benzyl-2-phenyl-2-thiazolinium bromide* (3). 3-Benzyl-2-phenyl-2-thiazolinium bromide (0·3 g.) in water (10 ml.) was refluxed for 5 min. The solvent was then removed to yield a gum, which gave *2-benzoylthioethyl(benzyl)ammonium bromide* (33) (0·17 g., 57%), m.p. 176—178° (from isobutyl alcohol) (Found: C, 54·6; H, 5·4; N, 3·7. $C_{16}H_{18}$BrNOS requires C, 54·5; H, 5·1; N, 4·0), $\nu_{max.}$ (Nujol) 2780, 2660, 2600, and 2450 ($\overset{+}{N}H_2$), and 1670 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 6·7 (2H, t, *J* 6·0 Hz, CH_2·S), 6·4 (2H, t, *J* 6·0 Hz, CH_2·$\overset{+}{N}$), 5·7 (2H, s, PhCH_2), and 2·0—2·7 (10H, m, 2 × Ph).

Ring opening of the salt (3) was more rapid than that of (2); no further change took place after *ca.* 6 hr. The relative proportions of unchanged salt (3) and of ring-opened material (33) were determined by comparison of the $C=\overset{+}{N}$ and C=O peaks in the i.r. spectrum: the ratio was found to be 1 : 1.

(iii) *3-Benzoyl-2-benzylthio-2-thiazolinium bromide* (9). 3-Benzoyl-2-benzylthio-2-thiazolinium bromide (0·5 g.) in aqueous ethanol (10 ml.) was heated under reflux for 10 min. On cooling, colourless crystals of *2-benzoylaminoethyl benzyl dithiocarbonate* (37) separated; m.p. 95° (Found: C, 61·8; H, 5·3; N, 4·0. $C_{17}H_{17}NO_2S_2$ requires C, 61·6; H, 5·2; N, 4·2%), $\nu_{max.}$ (Nujol) 3300 (NH) and 1650 and 1645 cm.$^{-1}$ (2 × C=O), τ ($CDCl_3$) 8·1 (1H, s, NH, exchangeable), 6·7 (2H, t, *J* 6·0 Hz, CH_2·S), 6·3 (2H, t, *J* 6·0 Hz, CH_2·N), 5·7 (2H, s, PhCH_2), 2·7 (5H, s, Ph), and 2·1—2·5 (5H, m, Ph).

(b) *Hydroxide ion.* (i) *3-Benzyl-2-methyl-2-thiazolinium bromide* (2). The thiazolinium salt (2·72 g., 1 mol.) was dissolved in water (50 ml.) and sodium hydroxide solution (4%; 10 ml., 1 mol.) was added. A gum separated which was extracted into ether; the extract was dried and evaporated to leave *N-acetyl-2-benzylaminoethanethiol* (38) as a gum (2·8 g., 95%), $\nu_{max.}$ 2550w (SH) and 1640s cm.$^{-1}$ (C=O), τ ($CDCl_3$) 8·0 (3H, s, Ac), 7·2 (2H, t, CH_2·S), 6·95 (1H, s, SH, exchangeable), 6·4 (2H, t, CH_2·N), 5·35 (2H, s, PhCH_2), and 2·6 (5H, s, Ph). The gum (1·05 g., 1 mol.) was dissolved in an excess of sodium hydroxide solution (4%) and to it was added a solution of *p*-nitrobenzyl bromide (1·08 g., 1 mol.) in ethanol (20 ml.). Solid which separated yielded the *p-nitrobenzyl thioether* (0·8 g., 40%), m.p. 85—86° (from propan-2-ol) (Found: C, 62·6; H, 5·8; N, 7·8. $C_{18}H_{20}$-

[17] G. Kumpf, *Annalen*, 1883, **224**, 99.
[18] G. I. Braz, *Zhur. obshchei Khim.*, 1951, **21**, 688.
[19] T. Wieland and E. Bokelmann, *Annalen*, 1952, **576**, 20.

N_2O_3S requires C, 62·8; H, 5·9; N, 8·1%), $\nu_{max.}$ (Nujol) 1640 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 7·8 (3H, s, Ac), 7·4 (2H, t, CH_2·S), 6·4 (2H, t, CH_2·N), 6·2 (2H, s, ArCH_2·S), 5·4 (2H, s, PhCH_2·N), 2·6 (5H, s, Ph), and 1·7—2·4 (4H, m, C_6H_4).

The gum (0·5 g.) was dissolved in ethanol and hydrobromic acid (1 mol.) was added. The solvent was then evaporated off to yield a gum which i.r. spectroscopy showed to be a mixture of 3-benzyl-2-methyl-2-thiazolinium bromide (2) and 2-acetylthioethyl(benzyl)ammonium bromide (32).

When 2-acetylthioethyl(benzyl)ammonium bromide (32) (1·45 g., 1 mol.) was dissolved in water and sodium hydroxide solution (4%; 5 ml., 1 mol.) was added, a gum separated. This was extracted with ether and the extract was dried ($MgSO_4$) and evaporated to yield compound (38) (i.r. spectrum identical with that of authentic material).

(ii) *3-Benzyl-2-phenyl-2-thiazolinium bromide* (3). The salt (1·67 g.), treated with aqueous sodium hydroxide as in (i), yielded *N-benzoyl-2-benzylaminoethanethiol* (39) as a sticky, hygroscopic solid, m.p. 40—45°, $\nu_{max.}$ (Nujol) 2550w (SH) and 1635 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 8·8 (1H, s, SH, exchangeable), 7·3 (2H, t, CH_2·S), 6·4 (2H, t, CH_2·N), 5·3 (2H, s, PhCH_2), and 2·5—2·6 (10H, m, 2 × Ph).

The thiol (1·36 g., 1 mol.) was dissolved in water (20 ml.) and aqueous sodium hydroxide (4%; 10 ml., 2 mol.) was added. The separated solid did not completely redissolve so ethanol (30 ml.) was added to produce an homogeneous solution. *p*-Nitrobenzyl bromide (1·08 g., 1 mol.) in ethanol (30 ml.) was then added. A yellow solid separated which yielded the p-*nitrobenzyl thioether* (1·5 g., 65%), m.p. 107—108° (from ethanol) Found: C, 67·8; H, 5·5; N, 7·1. $C_{23}H_{22}N_2O_3S$ requires C, 68·0; H, 5·5; N, 6·9%), $\nu_{max.}$ (Nujol) 1640 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 7·4 (2H, t, CH_2·S), 6·4 (2H, t, CH_2·N), 6·3 (2H, s, ArCH_2·S), 5·4 (2H, s, PhCH_2·N), 2·6 (10H, s, 2 × Ph), and 1·8—2·7 (4H, m, C_6H_4).

(iii) *3-Methyl-2-methylthio-2-thiazolinium iodide* (4). The salt (0·55 g., 1 mol.) was dissolved in water (10 ml.) and sodium hydroxide solution (4%; 2 ml., 1 mol.) was added. The separated oil was extracted into methylene dichloride and the extract was dried ($MgSO_4$) and evaporated to leave a gum (0·32 g.). T.l.c. (methylene dichloride) showed three spots; the mixture was separated by column chromatography on silicic acid with methylene dichloride as eluant. The first fraction yielded 3-methylthiazolidin-2-one (40) (0·18 g., 90%), $\nu_{max.}$ 1670 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 7·6 (3H, s, Me), 6·75 (2H, t, *J* 6 Hz, CH_2·S), and 6·4 (2H, t, *J* 6 Hz, CH_2·N), identical with authentic material.[20,21]

(iv) *3-(p-Nitrobenzyl)-2-(p-nitrobenzylthio)-2-thiazolinium bromide* (5). The salt (0·92 g., 1 mol.) was dissolved in dimethylformamide (20 ml.) and sodium hydroxide solution (4%; 2 ml., 1 mol.) was added. The red solution was evaporated (<40°) under reduced pressure and the residue was extracted with methylene dichloride. The extract was dried ($MgSO_4$) and evaporated to leave a gum, which yielded *3-(p-nitrobenzyl)thiazolidin-2-one* (41) (0·3 g., 65%), m.p. 137—138° (from ethanol) (Found: C, 50·2; H, 4·3; N, 11·8. $C_{10}H_{10}N_2O_3S$ requires C, 50·4; H, 4·2; N, 11·8%), $\nu_{max.}$ (Nujol) 1660 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 6·7 (2H, t, *J* 6·0 Hz, CH_2·S), 6·5 (2H, t, *J* 6·0 Hz, CH_2·N), 5·5 (2H, s, ArCH_2), and 1·8—2·5 (4H, m, C_6H_4).

(v) *2,3,5,6-Tetrahydrothiazolo*[2,3-b]*thiazolium bromide* (19). The salt (1·13 g., 1 mol.) was dissolved in water (10 ml.) and sodium hydroxide solution (4%; 5 ml., 1 mol.) was added. The separated oil was redissolved in sodium hydroxide solution (4%; 5 ml., 1 mol.) and hydrogen peroxide solution (20 vol.; 1 mol.) was added. Crystals which separated overnight yielded *bis-2-(2-oxothiazolidin-3-yl)-ethyl disulphide* [the disulphide of (42)] (0·3 g., 45%), m.p. 94—95° (from ethanol) (Found: C, 36·8; H, 4·9; N, 8·4. $C_{10}H_{16}N_2O_2S_4$ requires C, 37·0; H, 5·0; N, 8·6%), $\nu_{max.}$ (Nujol) 1655 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 7·1 (2H, t, CH_2·S·S), 6·7 (2H, t, CH_2·S·C=O), 6·4 (2H, t, CH_2·N), and 6·3 (2H, t, CH_2·N·C=O).

(vi) *2,3,6,7-Tetrahydro-5H-thiazolo*[2,3-b][1,3]*thiazinium bromide* (20). The salt (1·27 g.), treated similarly, yielded *bis-3-(2-oxothiazolidin-3-yl)propyl disulphide* [the disulphide of (43)] (0·25 g., 35%), m.p. 74—76° (from ethanol) (Found: C, 40·7; H, 5·6; N, 7·7. $C_{12}H_{20}N_2O_2S_4$ requires C, 40·9; H, 5·7; N, 7·9%), $\nu_{max.}$ (Nujol) 1655 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 8·0 (2H, quintet, C·CH_2·C), 7·3 (2H, t, C·C·CH_2·S), 6·7—6·4 (2H, t, C·C·CH_2·N), 6·7—6·4 (2H, t, CH_2·S), and 6·7—6·4 (2H, t, CH_2·N).

(c) *Borohydride ion.* (i) *3-Benzyl-2-methyl-2-thiazolinium Bromide* (2). The salt (1 g., 1 mol.) was dissolved in dimethylformamide (30 ml.) and a solution of sodium borohydride (0·38 g., 3 mol.) in dimethylformamide was added during 15 min. After 10 min. the pH was adjusted to 6 with dilute hydrobromic acid, the solvent was removed, and the residue was extracted with methylene dichloride The extract was dried ($MgSO_4$) and evaporated to yield a gum which on treatment with ethanolic picric acid yielded *3-benzyl-2-methylthiazolidine picrate*, m.p. 120—123° (from ethanol) (Found: C, 48·2; H, 4·3; N, 13·0. $C_{17}H_{18}N_4O_7S$ requires C, 48·3; H, 4·3; N, 13·3%), τ (CCl_4) (free base) 8·7 (3H, d, Me), 7·2 (4H, m, CH_2·CH_2), and 5·5 (1H, d, CH).

(ii) *3-Benzyl-2-phenyl-2-thiazolinium bromide* (3). The salt (1·67 g.), treated similarly, yielded *3-benzyl-2-phenylthiazolidine picrate*, m.p. 132—133° (Found: C, 54·4; H, 4·4; N, 11·8. $C_{22}H_{20}N_4O_7S$ requires C, 54·5; H, 4·2; N, 11·6%), τ ($CDCl_3$) (free base) 7·0 (4H, m, CH_2·CH_2), 6·4 (2H, ABq, *J* 14 Hz, PhCH_2), 4·8 (1H, d, CH), and 2·4—2·8 (10H, m, 2 × Ph). The AB quartet arises from the nonequivalence of the benzylic protons consequent on the slow inversion of the ring nitrogen atom.

(iii) *2,3,5,6-Tetrahydrothiazolo*[2,3-b]*thiazolium bromide* (19). The salt (1·13 g., 1 mol.) was added slowly to a solution of sodium borohydride (0·76 g., 4 mol.) in ethanol (50 ml.). The mixture was stirred (30 min.) and the pH was then adjusted to 3 with dilute hydrobromic acid. The solvent was removed, the residue was extracted with chloroform, and the extract was dried ($MgSO_4$) and evaporated to leave a solid which yielded *2,3,4,5,6,7a-hexahydrothiazolo*[2,3-b]*thiazolium bromide* (44) (0·8 g., 70%), m.p. 96—98° (from acetonitrile) (Found: C, 26·4; H, 4·7; N, 6·2; S, 28·3. $C_5H_{10}BrNS_2$ requires C, 26·3; H, 4·4; N, 6·1; S, 28·1%), τ ($CDCl_3$) 6·6 (8H, m, 2 × CH_2·CH_2), 5·8 (1H, NH, exchangeable), and 3·6 (1H, s, CH).

(iv) *2,3,6,7-Tetrahydro-5H-thiazolo*[2,3-b][1,3]*thiazinium bromide* (20). The salt (2·4 g.), treated similarly, yielded *2,3,4,6,7,7a-hexahydro-5H-thiazolo*[2,3-b][1,3]*thiazinium bromide* (45) (1·5 g., 60%), m.p. 162—164° (Found: C, 29·9; H, 4·8; N, 5·7; S, 26·3. $C_6H_{12}BrNS_2$ requires C, 29·8; H, 5·0; N, 5·8; S, 26·5%), τ (CF_3·CO_2H) 7·6 (2H, m, C·CH_2·C), 7·0 (2H, m, C·C·CH_2·S), 6·6 (2H, m, CH_2·S), 6·1 (2H, m, C·C·CH_2·$\overset{+}{N}$), 6·0 (2H, m, CH_2·$\overset{+}{N}$), 4·6 (1H, d, *J* 9·0 Hz, CH), and 3·9 (1H, d, *J* 2·0 Hz, CH). The two signals, with different coupling constants, ascribed to hydrogen on the

[20] K. K. Kuzmina, N. G. Ostroumova, Yu. V. Markova, and M. N. Shchukina, *Zhur. obshchei Khim.*, 1964, **34**, 987.
[21] H. Eilingsfield and L. Moebius, *Chem. Ber.*, 1965, **98**, 1293.

ring-junction carbon atom are thought to arise from *cis*- and *trans*-isomers, since on addition of deuterium oxide both signals remain but become singlets: the larger coupling constant probably arises from the *trans*-isomer.

(d) *Benzenethiolate ion.* (i) 3-*Benzyl*-2-*phenyl*-2-*thiazolinium bromide* (3). Sodium benzenethiolate (1·2 g., 1 mol.) in anhydrous ethanol (10 ml.) was added to a solution of the salt (3·0 g., 1 mol.) in anhydrous ethanol (30 ml.). The solvent was removed (30°, 1 mm.), the residue was extracted with methylene dichloride, and the solution was evaporated. The resultant solid yielded 3-*benzyl*-2-*phenyl*-2-*phenylthiothiazolidine* (48) (2 g., 65%), m.p. 88—89° (from methylene dichloride) (Found: C, 72·6 H, 5·9; N, 3·8; S, 17·5. $C_{22}H_{21}NS_2$ requires C, 72·7; H, 5·8; N, 3·9; S, 17·6%). The n.m.r. spectrum ($CDCl_3$) shows the presence of a mixture of two isomers in a ratio of *ca.* 2 : 1: major isomer τ 6·6 (2H, t, *J* 8·0 Hz, CH_2·S), 5·8 (2H, t, *J* 8·0 Hz, CH_2·N), 5·3 (2H, s, PhCH_2), and 2·7—2·8 (15H, m, 3 × Ph); minor isomer τ 7·1 (2H, t, *J* 8·0 Hz, CH_2·S), 6·4 (2H, t, *J* 8·0 Hz, CH_2·N), 4·6 (2H, s, PhCH_2), and 2·7—2·8 (15H, m, 3 × C_6H_5). In C_6D_6 (40°) the major isomer showed τ 6·7, 5·9, and 4·8; minor isomer τ 7·4, 6·7, and 5·6. At 60° all peaks were broadened; at 77° the spectrum showed broad peaks at τ 6·7, 5·9, and 5·6, *i.e.* coalescence had occurred.

(ii) 2,3,6,7-*Tetrahydro*-5H-*thiazolo*[2,3-b][1,3]*thiazinium bromide* (20). The salt (2 g.), treated similarly (24 hr.), yielded 2,3,6,7-*tetrahydro*-8a-*phenylthio*-5H,8aH-*thiazolo*[2,3-b][1,3]*thiazine* (47) (0·5 g., 20%), m.p. 108—110° (from ethanol) (Found: C, 53·4; H, 5·7; N, 4·9. $C_{12}H_{15}NS_3$ requires C, 53·5; H, 5·6; N, 5·2%), τ ($CDCl_3$) 7·8 (2H, quintet, C·CH_2·C), 7·1 (2H, t, C·C·CH_2·S), 6·6 (2H, t, C·CH_2·S), 6·4 (2H, t, C·C·CH_2·N), 5·8 (2H, t, C·CH_2·N), 2·5—2·8 (5H, m, Ph).

(iii) 2,3,5,6-*Tetrahydrothiazolo*[2,3-b]*thiazolium bromide* (19). The salt (1·5 g.), treated similarly (24 hr.), yielded 2,3,5,6-*tetrahydro*-7a-*phenylthio*-7aH-*thiazolo*[2,3-b]*thiazole* (46) (0·35 g., 20%), m.p. 80—81° (Found: C, 51·9; H, 4·9; N, 5·3. $C_{11}H_{13}NS_3$ requires C, 51·7; H, 5·1; N, 5·5%), τ ($CDCl_3$) 6·9 (4H, t, 2 × CH_2·S), 6·5 (4H, t, 2 × CH_2·N), and 2·6—2·4 (5H, m, Ph).

Similar treatment of the salt (1·5 g.) in methanol yielded 2,3,5,6-*tetrahydro*-7a-[2-(2-*oxothiazolidin*-3-*yl*)*ethylthio*]-7aH-*thiazolo*[2,3-b]*thiazole* (49) (0·5 g., 25%), m.p. 109—111° (Found: C, 38·8; H, 5·4; N, 9·4. $C_{10}H_{16}N_2OS_4$ requires C, 38·9; H, 5·2; N, 9·1%), $\nu_{max.}$ (Nujol) 1670 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 7·2 [2H, t, CH_2·S (open chain)] and 6·2—6·8 (14H, m).

The adduct (46) was decomposed by dilute acid to yield the original bicyclic salt (19), which was isolated as the picrate, m.p. and mixed m.p. 154—156°.

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