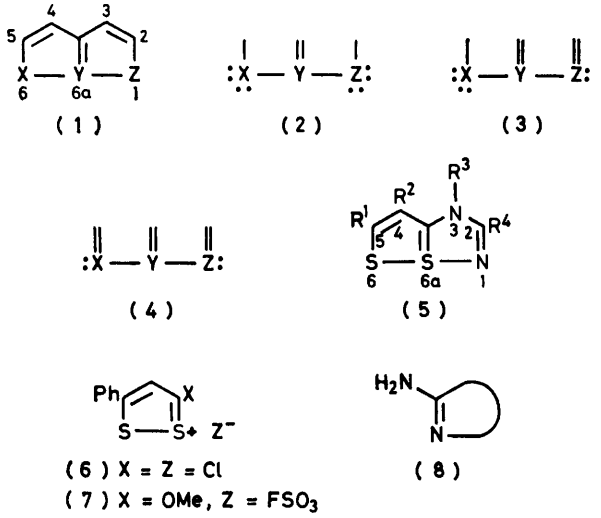
Studies of Heterocyclic Compounds. Part 28.[1] Condensation of 3-Substituted 5-Phenyl-1,2-dithiolylium Salts with 2-Amino-*N*-heterocycles

By **James A. Mitchell** and **David H. Reid,*** Department of Chemistry, The Purdie Building, The University, St. Andrews KY16 9ST, Scotland

3-Chloro-5-phenyl-1,2-dithiolylium chloride condenses in ethanol with 2-amino-*N*-heterocycles at the amino-group to yield yellow compounds; in many instances reaction occurs also at the ring nitrogen atom yielding orange compounds. 2-Amino-Δ^2-thiazoline, 2-aminothiazole, 2-aminopyridine and its monomethyl derivatives, 2-amino-4,6-dimethylpyridine, 2-aminopyrimidine, and 2-aminobenzimidazole all underwent reaction at the amino-group to give the corresponding yellow 2-(5-phenyl-1,2-dithiol-3-ylideneamino)-*N*-heterocycles. 2-Amino-Δ^2-thiazoline, 2-aminothiazole, 2-aminopyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, and 2-amino-5-methylpyridine also underwent reaction at the ring nitrogen atom to give in low yield 4,5-dihydro-3-thiobenzoylmethylene-3*H*-thiazolo[2,3-*c*][1,2,4]thiadiazole, 3-thiobenzoylmethylene-3*H*-thiazolo[2,3-*c*][1,2,4]-thiadiazole, and 3-thiobenzoylmethylene-3*H*-pyrido[2,1-*c*][1,2,4]thiadiazole and its 7-, 6-, and 5-methyl derivatives, respectively, as polar orange compounds. The condensations of 3-methoxy-5-phenyl-1,2-dithiolylium fluorosulphonate with 2-amino-Δ^2-thiazoline, 2-aminothiazole, and 2-amino-4-methylpyridine were studied. Condensation of 4-methyl-2-trichloromethylthioaminopyridine with benzoylacetic acid in dimethylformamide in the presence of triethylamine gave 6-methyl-3*H*-pyrido[2,1-*c*][1,2,4]thiadiazol-3-one (main product) and 6-methyl-3-benzoylmethylene-3*H*-pyrido[2,1-*c*][1,2,4]thiadiazole. Thionation of the latter with tetraphosphorus decasulphide in pyridine gave 6-methyl-3-thiobenzoylmethylene-3*H*-pyrido[2,1-*c*][1,2,4]thiadiazole. The results of ^{1}H n.m.r. spectral studies, and of *X*-ray crystallographic studies by other workers, are discussed in relation to the structure of the yellow and the orange series of condensation products. It is proposed that the 3-thiobenzoylmethylene-3*H*-thiazolo[2,3-*c*][1,2,4]thiadiazoles and the 3-thiobenzoylmethylene-3*H*-pyrido[2,1-*c*][1,2,4]-thiadiazoles, whose formation involves an S–S ⟶ S–N bond switch, are formed *via* 3*H*-6,6aλ^4-dithia-1,3-diazapentalenes which are higher energy intermediates or transition states. 3-Chloro-5-phenyl-1,2-dithiolylium chloride condensed with 2,6-diaminopyridine in a 2 : 1 ratio to give an orange and a polar red product for which structures are proposed.

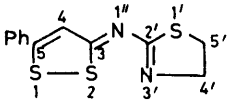
1,6,6aλ^4-TRIHETERAPENTALENES comprise a large number of compounds based on structure (1), in which Y = S, Se, or Te, and X and Z are O, S, Se, or NR. Many aza-analogues of (1) are known in which one or more ring carbon atoms at positions 2, 3, 4, and 5 are replaced by nitrogen atoms. The essential structural feature of 1,6,6aλ^4-triheterapentalenes is the heteroatom unit (2) which employs four-electron three-centre bonding. We can regard Y as having a singly occupied p_z orbital and X and Z as having a doubly occupied p_z orbital available for p_π–p_π conjugative interaction with neighbouring ring atoms. Variations of the triheterapentalene structure can be formulated which contain the structural elements



(3) or (4). In (3), Y and Z can be regarded as possessing a singly occupied p_z orbital and X a doubly occupied p_z orbital. In (4), X, Y, and Z can be considered to have singly occupied p_z orbitals. Authentic examples of compounds containing unit (3) or (4) have not been reported hitherto, although it has been suggested that structures containing these units are intermediates in several reactions.[2] We now report the results of attempts to synthesise 3*H*-6,6aλ^4-dithia-1,3-diazapentalenes (5), which contain unit (3; X = Y = S, Z = N), by the reaction of the 1,2-dithiolylium salts (6) and (7) with 2-amino-*N*-heterocycles (8).

Condensation of the 1,2-*Dithiolylium Salts* (6) *and* (7) *with* 2-*Amino*-N-*heterocycles*.—Condensation of 3-chloro-5-phenyl-1,2-dithiolylium chloride (6) with 2-amino-Δ^2-thiazoline, 2-aminothiazole, 2-aminopyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, and 2-amino-5-methylpyridine in ethanol and subsequent chromatography gave in each case two isomeric condensation products: a faster running yellow compound and a polar orange compound. The salt (6) also reacted with 2-amino-6-methylpyridine, 2-amino-4,6-dimethylpyridine, 2-aminopyrimidine, and 2-aminobenzimidazole to give only a yellow condensation product. For reasons given subsequently, we conclude that the yellow compounds result from condensation at the amino-substituent and possess structures (9)—(18), and that the polar orange compounds result from reaction at the ring nitrogen atom of the 2-amino-*N*-heterocycle (8) and possess structures (19)—(24).

In all these reactions the thione (25) and the ketone (26) were produced in substantial amount [(25), 5.8—



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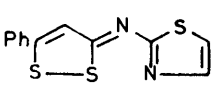

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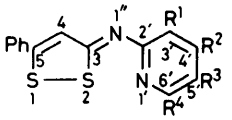
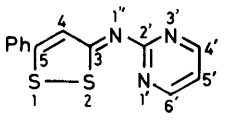


	R^1	R^2	R^3	R^4
(11)	H	H	H	H
(12)	Me	H	H	H
(13)	H	Me	H	H
(14)	H	H	Me	H
(15)	H	H	H	Me
(16)	H	Me	H	Me



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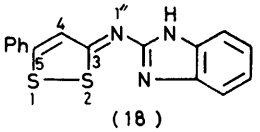

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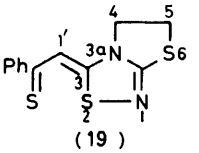

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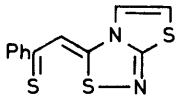

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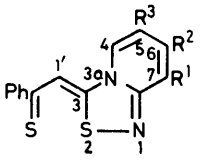
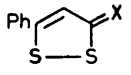


	R^1	R^2	R^3
(21)	H	H	H
(22)	Me	H	H
(23)	H	Me	H
(24)	H	H	Me

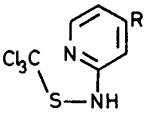


(25) X = S
(26) X = O

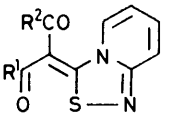
27%; (26), 25—44%] by a competing solvolysis of the dithiolylium chloride (6), and in the majority of the reactions the ketone (26) was the major product. Consequently yields of the condensation products were at best only moderate. Yields of the yellow compounds varied widely (3.3—41%), and the orange isomers, when formed, were present in very small quantities (0.2—4.9%). The use of dimethylformamide, hexamethylphosphoric triamide, methanol, or benzene in place of ethanol in the condensation of the salt (6) with 2-amino-Δ^2-thiazoline resulted in reduced yields of both products (9) and (19). The use of acetonitrile tripled the yield of the yellow product but diminished that of the orange isomer (19). The effect of using the dithiolylium salt (7), obtained by methylation of the ketone (26) with methyl fluorosulphonate in benzene, in place of the chloride (6) was investigated. 2-Amino-Δ^2-thiazoline gave a greatly improved yield (3.6% ⟶ 10.3%) of the orange product (19) but none of the yellow isomer (9), while 2-aminothiazole and 2-amino-4-methylpyridine gave poorer yields of both condensation products (10) and (20), and (13) and (23), respectively.

The failure of 2-amino-6-methylpyridine and 2-amino-4,6-dimethylpyridine to give orange condensation products corresponding to compounds (21)—(24) is doubtless due to the additional blocking of the ring nitrogen atom by the 6-methyl substituent.

Synthesis of 6-Methyl-3-thiobenzoylmethylene-3H-pyrido[2,1-c][1,2,4]thiadiazole (23) *from 4-Methyl-2-trichloromethylthioaminopyridine* (28).—At an early stage of



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



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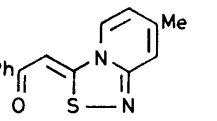

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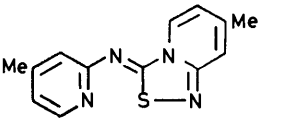

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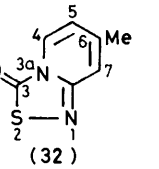
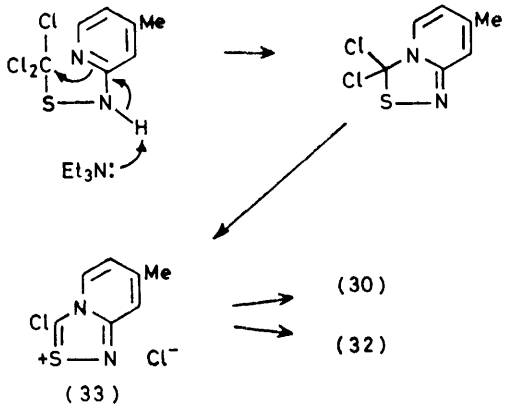


(32)

this work we sought evidence from synthesis that the polar orange products result from condensation of the 1,2-dithiolylium ion with the 2-amino-*N*-heterocycle (8) at the ring nitrogen atom. Since it has been shown [3] that the sulphenamide (27) [4] condenses with the carbanions of 1,3-dicarbonyl compounds in ethanol to give pyrido[2,1-*c*][1,2,4]thiadiazoles (29) (30—50%), we decided to synthesise the ketone (30) by condensation of the sulphenamide (28) with benzoylacetic acid. Attempted condensations in ethanol or aqueous ethanol in the presence of sodium hydroxide and sodium carbonate (*cf.* ref. 3) gave mainly the pyrido[2,1-*c*][1,2,4]thiadiazole (31) (70—84%) and less than 1% of compound (30). We succeeded in obtaining compound (30) in low yield (8.2%) along with the major product (32) (49%) by carrying out the condensation in dimethylformamide in the presence of triethylamine. Formation of compound (31) in protogenic solvents doubtless results from the condensation of 2-amino-4-methylpyridine with the sulphenamide (28) (*cf.* ref. 3), the 2-amino-4-methylpyridine having been formed previously from the sulphenamide (28) by nucleophilic attack at the sulphur atom. It is possible that in dimethylformamide the ketone (32) and compound (30) are formed *via* an intermediate pyrido-[2,1-*c*][1,2,4]thiadiazolylium salt (33) (Scheme 1). Hydrolysis of this salt would give the ketone (32), and condensation with the carbanion of benzoylacetic acid would yield compound (30).

Thionation of compound (30) with tetraphosphorus decasulphide in pyridine gave the same polar orange compound (23) as had been obtained from the condensation of the salt (6) with 2-amino-4-methylpyridine. The orange product from the condensation of the salt (6) with 2-amino-4-methylpyridine must therefore have resulted from reaction at the ring nitrogen atom. We assume that the other orange condensation products

[(19)—(22) and (24)] also arise by reaction of the salt (6) with the 2-amino-*N*-heterocycles at the ring nitrogen atom. It follows that the yellow series of condensation products [(9)—(18)] are formed by reaction of the salts



SCHEME 1

(6) and (7) with the 2-amino-*N*-heterocycles at the amino-substituent. The results of ^{1}H n.m.r. and *X*-ray crystallographic studies support and amplify these conclusions.

Structures of the Yellow and the Orange Products from the Condensation of the 1,2-*Dithiolylium Salts* (6) *and* (7) *with* 2-*Amino*-N-*heterocycles.*—Compounds (14) and (19), representing the yellow and the orange series of condensation products, formed crystals suitable for *X*-ray single-crystal structure determinations. Details of the structure determinations have been published,[5,6] and only essential data are discussed here.

In compound (14) the dithiole and the pyridine rings are nearly coplanar, with the ring nitrogen atom lying close to the extended S–S bond axis. The S···S (2.155 Å) and the S···N (2.282 Å) distance in compound (14) are,[5] respectively, much shorter and much

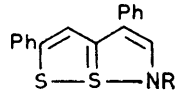
TABLE 1

S–S and S–N bond lengths (Å) in the 1,6,6aλ^4-triheterapentalenes (34—(39)

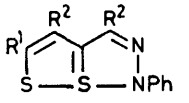
Compound	S–S	S–N
(34) [a]	2.396	1.871
(35) [b]	2.364	1.887
(36) [c]	2.435	1.849
(37) [d]	2.493	1.779
(38) [e]	2.494	1.814
(39) [f]	2.447	1.863

[a] F. Leung and S. C. Nyburg, *Can. J. Chem.*, 1972, **50**, 324; [b] F. Leung and S. C. Nyburg, *Can. J. Chem.*, 1971, **49**, 167; [c] L. K. Hansen and K. Tomren, *Acta Chem. Scand., Ser. A*, 1977, **31**, 292; [d] L. P. Darmo and L. K. Hansen, *Acta Chem. Scand., Ser. A*, 1977, **31**, 412; [e] L. K. Hansen, *Acta Chem. Scand., Ser. A*, 1981, **35**, 61; [f] L. K. Hansen, *Acta Chem. Scand., Ser. A*, 1977, **31**, 855.

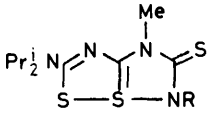
longer than the corresponding distances in 1,6,6aλ^4-triheterapentalenes containing the S–S–N sequence. The S–S and S–N bond lengths in compounds (34)—(39) lie in the range 2.494—2.364 and 1.887—1.779 Å, respectively (Table 1). The S···S distance in compound (14) is only slightly longer than the two-electron covalent S–S bond length (*ca.* 2.08 Å). These results support the 2-(1,2-dithiol-3-ylideneamino)pyridine structure (14) rather than the triheterapentalene structure (40). The slight lengthening of the S–S bond suggests that a weak bonding interaction exists between S(2) and N(1′), sufficient to hold the molecule in the observed configuration. It seems reasonable also to formulate the yellow compounds (9)—(13) and (15)—(18) as 2-(1,2-dithiol-3-ylideneamino)-*N*-heterocycles. The aromatic stabilisation energy associated with the thiazole, pyridine, pyrimidine, and imidazole rings may be an important factor favouring the 2-(1,2-dithiol-3-ylideneamino)-*N*-heterocycle structures over the triheterapentalene structures. If so, the yellow product



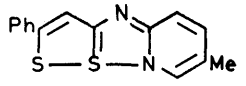
(34) R = Ph
(35) R = 3-Quinolinyl



(36) R¹ = Bu^t, R² = H
(37) R¹ = H, R² = Me



(38) R = Me
(39) R = Ph



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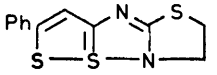


(41)

(9) from 2-amino-Δ^2-thiazoline might require to be reformulated as the triheterapentalene (41).

The 4-H signal in the ^{1}H n.m.r. spectra of compounds (9)—(17) in [^{2}H]chloroform (see Table 2) occurs in the narrow range δ 7.48—7.72. This suggests that all these compounds have the same configuration about the C(3)–N(1″) bond, with the nitrogen-containing ring remote from 4-H.

The results of a variable-temperature ^{1}H n.m.r. spectral study of compound (17) show that any S···N bonding interaction in compound (17) must be very small. At —24 °C the spectrum in [^{2}H]chloroform shows a two-proton doublet at δ 8.81 arising from 4′-H and 6′-H, and a one-proton triplet at δ 7.05 arising from 5′-H (J 4.9 Hz). These data show that 4′-H and 6′-H are magnetically equivalent and consequently that there is free rotation about the C(2′)–N(1″) bond. At 31 °C the signal from 4′-H and 6′-H was a poorly resolved triplet and that from 5′-H had become a broad singlet ($W_{\frac{1}{2}}$ *ca.* 20 Hz). This change in pattern with increasing temperature is doubtless due to the onset of free rotation about the C(3)–N(1″) bond.

The similarity in structure of compounds (9)—(18) is also suggested by the u.v.–visible spectra, which show

TABLE 2

^{1}H N.m.r. spectral data for compounds (9)—(17) in [^{2}H]-chloroform, compound (18) in [$^2H_6$]dimethyl sulphoxide, and compounds (19)—(21), (23), and (30) in [$^2H_5$]pyridine

Compound	δ Values; J in Hz
(9)	3.53 (2 H, t, 5′-H_2), 4.33 (2 H, t, 4′-H_2), 7.40—7.48 (3 H, m, 2 *m*- + *p*-protons of 5-Ph), 7.53 (1 H, 4-H), 7.63—7.74 (2 H, m, 2 *o*-protons of 5-Ph)
(10)	7.08 (1 H, d, 5′-H), 7.45—7.53 (3 H, m, 2 *m*- + *p*-protons of 5-Ph), 7.48 (1 H, 4-H), 7.62—7.76 (2 H, m, 2 *o*-protons of 5-Ph), 7.67 (1 H, d, 4′-H); $J_{4',5'}$ 3.9
(11)	7.03 (1 H, ddd, 5′-H), 7.35—7.45 (4 H, m, 3′-H and 2 *m*- + *p*-protons of 5-Ph), 7.61 (1 H, 4-H), 7.64—7.85 (3 H, m, 4′-H and 2 *o*-protons of 5-Ph), 8.47 (1 H, ddd, 6′-H); $J_{4',5'}$ 7.6, $J_{5',6'}$ 5.4
(12)	2.51 (3 H, 3′-Me), 6.97 (1 H, dd, 5′-H), 7.36—7.45 (3 H, m, 2 *m*- + *p*-protons of 5-Ph), 7.55 (1 H, d,[a] 4′-H), 7.67—7.80 (2 H, m, 2 *o*-protons of 5-Ph), 7.71 (1 H, 4-H), 8.31 (1 H, d,[b] 6′-H); $J_{4',5'}$ 7.8, $J_{4',6'}$ 1.6, $J_{5',6}$ 5.3
(13)	2.37 (3 H, br, 4′-Me), 6.89 (1 H, ddq, 5′-H), 7.21 (1 H, br, 3′-H), 7.37—7.48 (3 H, m, 2 *m*- + *p*-protons of 5-Ph), 7.59 (1 H, 4-H), 7.67—7.77 (2 H, m, 2 *o*-protons of 5-Ph), 8.34 (1 H, d, 6′-H); $J_{3',5'}$ 1.6, $J_{3',6'}$ 0.8, $J_{5',6'}$ 5.4
(14)	2.32 (3 H, 5′-Me), 7.35—7.76 (7 H, m, 3′-H + 4′-H + 5-Ph), 7.58 (1 H, 4-H, 8.30 (1 H, br, 6′-H)
(15)	2.69 (3 H, 6′-Me), 6.92 (1 H, d, 5′-H), 7.30 (1 H, d, 3′-H), 7.41—7.52 (3 H, m, 2 *m*- + *p*-protons of 5-Ph), 7.63—7.82 (3 H, m, 4′-H and 2 *o*-protons of 5-Ph), 7.67 (1 H, 4-H); $J_{3',4'}$ 8.5, $J_{4',5'}$ 7.4
(16)	2.32 (3 H, 4′-Me), 2.59 (3 H, 6′-Me), 6.69 (1 H, br, 5′-H), 7.03 (1 H, br, 3′-H), 7.35—7.46 (3 H, m, 2 *m*- + *p*-protons of 5-Ph), 7.59 (1 H, 4-H), 7.65—7.77 (2 H, m, 2 *o*-protons of 5-Ph); $J_{3',5'}$ 1.5
(17) [c]	7.02 (1 H, t,[a,d] 5′-H), 7.44—7.54 (3 H, m, 2 *m*- + *p*-protons of 5-Ph), 7.66—7.76 (2 H, m, 2 *o*-protons of 5-Ph), 7.72 (1 H, 4-H), 8.80 (2 H, vbr,[e] 4′- and 6′-H)
(17) [f]	7.05 (1 H, t, 5′-H), 7.44—7.54 (3 H, m, 2 *m*- + *p*-protons of 5-Ph), 7.66—7.76 (2 H, m, 2 *o*-protons of 5-Ph), 7.72 (1 H, 4-H), 8.81 (2 H, d, 4′- and 6′-H); $J_{4'(6'),5'}$ 4.9
(18)	7.10—7.90 (9 H, m, benzene rings), 7.78 (1 H, 4-H), 12.38 (1 H, br, NH)
(19)	3.83 (2 H, dt, 5-H_2), 4.38 (2 H, dt, 4-H_2), 7.32—7.44 (3 H, m, 2 *m*- + *p*-protons of Ph), 7.62 (1 H, 1′-H), 8.07—8.18 (2 H, m, 2 *o*-protons of Ph)
(20)	7.34—7.46 (4 H, m, 5-H and 2 *m*- + *p*-protons of Ph), 8.08—8.20 (2 H, m, 2 *o*-protons of Ph), 8.37 (1 H, 1′-H), and 8.56 (1 H, d, 4-H); $J_{4,5}$ 4.9
(21)	8.40 (1′-H) [g]
(23)	2.16 (3 H, d, 6-Me), 6.66 (1 H, dd, 5-H), 7.24 (1 H, br, 7-H), 7.32—7.46 (3 H, m, 2 *m*- + *p*-protons of Ph), 8.17—8.28 (2 H, m, 2 *o*-protons of Ph), 8.45 (1 H, 1′-H), 8.82 (1 H, d, 4-H); $J_{4,5}$ 7.5, $J_{5,7}$ 1.9, $J_{6\text{-Me},7}$ 1.3
(30) [h]	2.07 (3 H, d, 6-Me), 6.38 (1 H, dd, 5-H), 6.98 (1 H, br, 7-H), 7.32—7.47 (4 H, m, 1′-H and 2 *m*- + *p*-protons of Ph), 8.11—8.24 (3 H, m, 4-H and 2 *o*-protons of Ph); $J_{4,5}$ 7.5, $J_{5,7}$ 1.7, $J_{6\text{-Me},7}$ 1.3

[a] Components broadened. [b] Components further split. [c] 31 °C. [d] Poorly resolved. [e] $W_{\frac{1}{2}}$ *ca.* 20 Hz. [f] −24 °C. [g] Other δ values not obtainable owing to decomposition. [h] 80 °C.

three principal regions of absorption in the ranges 414—387 (log ε 4.34—4.17), 295—284 (4.44—4.21), and 213—206 nm (4.80—4.41) (see Table 3).

The S···S (2.750 Å) and the S···N (1.727 Å) distances found [6] in compound (19) are, respectively, much longer and much shorter than the S–S and S–N bond lengths in the 1,6,6aλ^4-triheterapentalenes (34)—(39).

TABLE 3

U.v.–visible spectral data for compounds (9)—(17) in cyclohexane and compounds (18)—(20), (23), (30), (52), and (53) in methanol

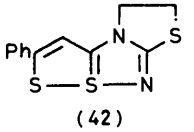
Compound	$\lambda_{max.}$/nm (log ε)
(9)	387 (4.34), 284 (4.44), 235sh (4.42), 211 (4.80)
(10)	430sh (4.13), 413 (4.19), 290 (4.23), 206 (4.43)
(11)	442sh (3.83), 415 (4.17), 402 (4.17), 286 (4.21), 271sh (4.18), 230sh (4.29), 212 (4.52)
(12)	444sh (3.88), 419 (4.17), 407 (4.17), 287 (4.21), 270 (4.19), 230sh (4.29), 211 (4.52)
(13)	442sh (3.82), 414 (4.17), 401 (4.17), 285 (4.24), 272sh (4.20), 230sh (4.36), 211 (4.60)
(14)	444sh (3.82), 416sh (4.16), 404 (4.18), 284 (4.24), 273sh (4.23), 231sh (4.31), 213 (4.51)
(15)	444sh (3.86), 415 plateau (4.17), 404 (4.17), 288 (4.23), 270 (4.20), 230sh (4.31), 212 (4.54)
(16)	444sh (3.84), 416sh (4.16), 405 (4.17), 287 (4.23), 272 (4.20), 230sh (4.35), 214 (4.56)
(17)	425sh (3.87), 406 (4.18), 394sh (4.16), 291 (4.21), 225sh (4.36), 210 (4.41)
(18)	414 (4.30), 295 (4.32), 225sh (4.42), 212 (4.63)
(19) [a]	417, 321, 279, 233, 205sh
(20) [a]	447, 325, 279, 238, 204
(23) [a]	457, 323, 279, 248, 213
(30)	409 (4.31), 366sh (3.93), 239sh (4.27), 226 (4.35), 206 (4.19)
(52)	399 (4.31), 291 (4.55), 210 (4.63)
(53) [a]	500, 334, 288, 225

[a] Log ε not determined owing to low solubility.

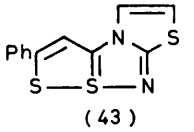
The S···N distance in compound (19) lies in the range found for heteroaromatic S–N two-electron covalent bond lengths. These results establish the 3-thiobenzoylmethylene-3*H*-thiazolo[2,3-*c*][1,2,4]thiadiazole structure (19) in which there is little S–S bonding, rather than the 3*H*-6,6aλ^4-dithia-1,3-diazapentalene structure (42). It seems reasonable to assume that the orange products from 2-aminothiazole and the 2-aminopyridines possess structures (20) and (21)—(24) rather than the corresponding 3*H*-6,6aλ^4-dithia-1,3-diazapentalene structures (43) and (44).

The most notable feature of the ^{1}H n.m.r. spectra of compounds (19)—(21) and (23) in [$^2H_5$]pyridine (see Table 2) is the position of the 1′-H signal. The 1′-H signal from compound (19) occurs at δ 7.62, but that from compounds (20), (21), and (23), in which an additional thiazole or pyridine ring-current effect operates, is found at much lower field (δ 8.37—8.45). This difference reflects the proximity of 1′-H to the ring originating from the 2-amino-*N*-heterocycle.

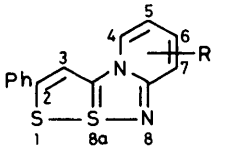
The foregoing results show that the formation of the orange condensation products (19)—(24) involves the



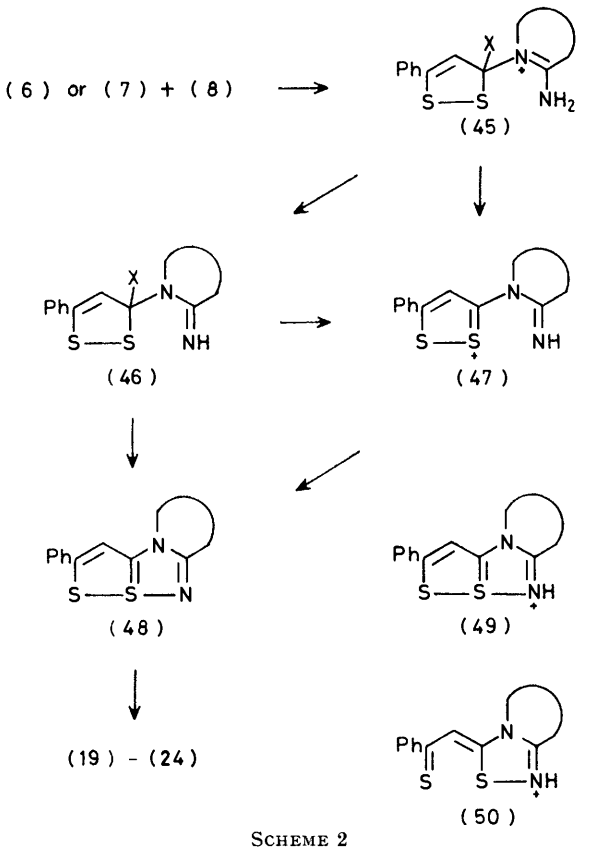
(42)



(43)

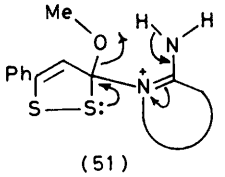


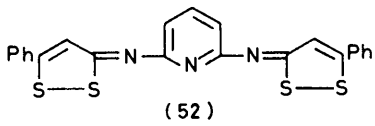
(44) R = H,7-,6-, or 5-Me

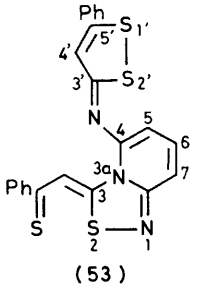


SCHEME 2

breaking of a ring S–S bond and the formation of a ring S–N bond. We propose that compounds (19)—(24) are formed *via* the intermediates (45)—(48) (Scheme 2). Formation of (48) from (46) could take place *via* (47) by the successive loss of X^- and H^+, or directly by a concerted loss of HX. Proton loss is assisted by the solvent


(51)


(52)


(53)

and the 2-amino-*N*-heterocycle (8) is present in excess. The intermediate (47) could be formed directly from (45; X = OMe) by a concerted loss of methanol *via* a six-membered transition state [see (51)]. Alternative pathways involving charged species (49) and (50) [(47) → (49) → (48) → (19)—(24) and (47) → (49) → (50) → (19)—(24)] seem less likely but at present cannot be discounted. Thus the 3*H*-6,6aλ^4-dithia-1,3-diazapentalenes (48), which contain unit (3; X = Y = S, Z = N), are not isolable compounds but may be higher-energy intermediates or transition states on the way to the products (19)—(24).

Condensation of 3-*Chloro*-5-*phenyl*-1,2-*dithiolylium Chloride* (6) *with* 2,6-*Diaminopyridine*.—Condensation of the salt (6) with 2,6-diaminopyridine in ethanol gave in low yield an orange compound and a polar red compound. Owing to the low solubility of these compounds we have been unable to obtain useful ^{1}H n.m.r. spectral information, but analytical and mass spectral data show that both compounds are derived from two molecules of the salt (6) and one molecule of 2,6-diaminopyridine. We provisionally assign structures (52) and (53) to the orange and the red compound, respectively.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. ^{1}H N.m.r. spectra were determined at 100 MHz for 0.4M-solutions in deuteriochloroform, unless otherwise indicated, with tetramethylsilane as internal reference. Unless otherwise stated, δ values refer to singlet absorptions. *J* Values were measured on the 100 Hz scale. Solutions were dried over sodium sulphate and evaporated at reduced pressure. Column chromatography was carried out with alumina (activity II—III, pH *ca.* 9.5, 70—230 mesh) or silica (85—200 mesh), unless otherwise indicated. Light petroleum was of boiling range 40—60 °C. Throughout ether denotes diethyl ether. Solvent mixtures are described in ratios by volume. The following abbreviations are used: B = benzene, E = diethyl ether, M = methanol, P = light petroleum. Reaction products were shown to be identical with authentic samples by m.p. and mixed m.p. determinations, and by showing that they had the same ^{1}H n.m.r. and mass spectra and displayed the same t.l.c. behaviour on silica as the authentic samples. MeOH–$HClO_4$ denotes a 1% (v/v) solution of 70% (w/w) perchloric acid in methanol. Dimethylformamide was dried for 1 week with powdered calcium hydride and then distilled at 15 mmHg. 3-Chloro-5-phenyl-1,2-dithiolylium chloride was prepared from 5-phenyl-1,2-dithiol-3-one [7] by the method of Mayer and Faust.[8]

3-*Methoxy*-5-*phenyl*-1,2-*dithiolylium Fluorosulphonate* (7). —Methyl fluorosulphonate (12.1 ml, 150 mmol) was added to a solution of 5-phenyl-1,2-dithiol-3-one (9.72 g, 50 mmol) in benzene (25 ml), and the resulting solution was boiled (oil-bath) for 30 min. The white solid which gradually separated was filtered off, washed with benzene and then with ether, and dried *in vacuo*. 3-*Methoxy*-5-*phenyl*-1,2-*dithiolylium fluorosulphonate* (12.46 g, 81%) was obtained as spars from acetonitrile, m.p. 110—112 °C (Found: C, 39.0; H, 3.2. $C_{10}H_9FO_4S_3$ requires C, 39.0; H, 2.9); $\lambda_{max.}$ (MeOH–$HClO_4$) 325 (log ε 4.33), 291 (4.40), and 208 nm (4.41); δ (CF_3CO_2H) 4.69 (3 H, OMe), 7.60—8.02 (5 H, m, Ph), and 8.03 (1 H, 4-H).

Condensation of 3-*chloro*-5-*phenyl*-1,2-*dithiolylium Chloride* (6) *with* 2-*Amino*-N-*heterocycles in Ethanol*.—The following general procedure was used. The 2-amino-*N*-heterocycle (20 mmol) was dissolved in ethanol (50 ml), and the dithiolylium salt (6) (2.49 g, 10 mmol) was washed into the solution with ethanol (10 ml). The mixture was boiled for 10 min, cooled, and poured into saturated aqueous sodium carbonate (300 ml). The resulting mixture was extracted with benzene (2 × 500 ml), and the extracts were washed with water (3 × 500 ml), dried, and evaporated. The residue was dissolved in benzene and chromatographed. The thione (25) was invariably the first product to be eluted, and was usually followed by the ketone (26). The chromatographic procedure for the complete separation of the thione (25) and the ketone (26) was similar for most reactions and is described in detail only in the case of the products from the reaction of the salt (6) with 2-amino-Δ^2-thiazoline. Procedures for the isolation of the other reaction product(s) varied and are given individually.

With 2-*amino*-Δ^2-*thiazoline*. Chromatography [alumina (50 × 2.8 cm)] gave the following fractions: (i) PB (3 : 1), 200 ml, pink (discarded); (ii) PB (2 : 1), 800 ml, orange; (iii) PB (2 : 1), 200 ml, orange, mixture; (iv) PB (1 : 1), 500 ml, colourless; (v) B, 550 ml, yellow; and (vi) BE (9 : 1), 700 ml, orange. Rechromatography [alumina (30 × 2.0 cm)] of fraction (iii) gave fractions (iii) (a) PB (3 : 1), 200 ml, orange; (iii) (b) PB (2 : 1), 200 ml, colourless; and (iii) (c) PB (1 : 1), 200 ml, colourless. Combination of fractions (ii) and (iii) (a) gave 5-phenyl-1,2-dithiol-3-thione (25) (562 mg, 27%), bronze plates from benzene, m.p. 125—126 °C (lit.,[7] 125—127 °C) (Found: C, 51.1; H, 2.9. Calc. for $C_9H_6S_3$: C, 51.4; H, 2.9%); δ 7.41—7.73 (m, 4-H and 5-Ph). Combination of fractions (iv), (iii) (b), and (iii) (c) gave 5-phenyl-1,2-dithiol-3-one (26) (416 mg, 21%), straw-coloured needles from cyclohexane, m.p. 115—117 °C (lit.,[7] 114—117 °C) (Found: C, 55.4; H, 3.0. Calc. for $C_9H_6OS_2$: C, 55.6; H, 3.1%); δ 6.81 (1 H, 4-H) and 7.42—7.67 (5 H, m, Ph). Rechromatography [alumina (20 × 2.0 cm)] of fraction (v) with benzene gave yellow eluates which afforded 4,5-*dihydro*-2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)*thiazole* (9) (91 mg, 3.3%), yellow needles from cyclohexane, m.p. 126 °C, *m/z* 278.0008 (M^+) (Found: C, 52.0; H, 3.5; N, 10.1; S, 34.7. $C_{12}H_{10}N_2S_3$ requires C, 51.8; H, 3.6; N, 10.1; S, 34.6%). Rechromatography [alumina (30 × 2.0 cm)] of fraction (vi) with benzene–ether (9 : 1) brought through orange eluates which yielded 4,5-*dihydro*-3-*thiobenzoylmethylene*-3H-*thiazolo*[2,3-c][1,2,4]*thiadiazole* (19) (99 mg, 3.6%), orange prisms from benzene, m.p. 202—203 °C, *m/z* 278.0000 (M^+) (Found: C, 51.6; H, 3.6; N, 10.1; S, 34.4. $C_{12}H_{10}N_2S_3$ requires C, 51.8; H, 3.6; N, 10.1; S, 34.6%).

With 2-*aminothiazole*. Chromatography [alumina (20 × 2.7 cm)] gave the following fractions: (i) PB (1 : 1), 250 ml, yellow, mixture; (ii) BE (9 : 1), 50 ml, red (discarded); and (iii) BE (9 : 1), 500 ml, red. Rechromatography [alumina; activity I, neutral, 80—200 mesh (50 × 2.7 cm)] of fraction (i) gave fractions (i) (a) PB (1 : 1), 21, yellow; (i) (b) PB (1 : 2), 200 ml, yellow; (i) (c) B, 200 ml, yellow, mixture (discarded); (i) (d) BE (9 : 1), 1.51, yellow; and (i) (e) BE (5 : 1), 300 ml, yellow, mixture (discarded). Fractions (i) (a) and (i) (b) gave the thione (25) (173 mg, 8.2%). Rechromatography [alumina (40 × 2.0 cm)] of fraction (i) (d) with petroleum–benzene (2 : 1) gave yellow eluates which afforded 2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)*thiazole* (10) (565 mg, 20%), orange plates from cyclohexane, m.p. 165—167 °C, *m/z* 275.9858 (M^+) (Found: C, 52.1; H, 3.0; N, 10.1. $C_{12}H_8N_2S_3$ requires C, 52.2; H, 2.9; N, 10.1%). Rechromatography [alumina (20 × 2.0 cm)] of fraction (iii) gave successively pale yellow eluates [PB (1 : 2)] which were discarded, and orange eluates [BE (9 : 1)] which yielded 3-*thiobenzoylmethylene*-3H-*thiazolo*[2,3-c][1,2,4]*thiadiazole* (20) (136 mg, 4.9%), red plates from benzene, m.p. 180—182 °C, *m/z* 275.9845 (M^+) (Found: C, 52.1; H, 2.9; N, 10.3. $C_{12}H_8N_2S_3$ requires C, 52.2; H, 2.9; N, 10.1%).

With 2-*aminopyridine*. Chromatography [alumina (50 × 2.7 cm)] gave the following fractions: (i) PB (3 : 1), 50 ml, purple (discarded); (ii) PB (3 : 1), 900 ml, orange; (iii) PB (3 : 1), 250 ml, orange, mixture; (iv) PB (1 : 1), 700 ml, colourless; (v) B, 800 ml, yellow; and (vi) BE (4 : 1), 400 ml, orange. Fractions (ii)—(iv) yielded the thione (25) (141 mg, 7.6%) and the ketone (26) (647 mg, 33%). Rechromatography [alumina (40 × 2.7 cm)] of fraction (v) gave successively brown eluates [PB (1 : 2)] which were discarded, and yellow eluates (B) which afforded 2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)*pyridine* (11) (1.118 g, 41%), yellow needles from cyclohexane, m.p. 133—133.5 °C, *m/z* 270.0295 (M^+) (Found: C, 62.1; H, 3.8; N, 10.4. $C_{14}H_{10}N_2S_2$ requires C, 62.2; H, 3.7; N, 10.4%). Rechromatography [alumina (20 × 1.5 cm)] of fraction (vi) with benzene–ether (9 : 1) yielded 3-*thiobenzoylmethylene*-3H-*pyrido*[2,1-c][1,2,4]*thiadiazole* (21) (67 mg, 2.5%) as a viscous red oil which failed to crystallise, *m/z* 270.0295 (M^+) (Found: C, 61.8; H, 3.4; N, 10.3. $C_{14}H_{10}N_2S_2$ requires C, 62.2; H, 3.7; N, 10.4%).

With 2-*amino*-3-*methylpyridine*. Chromatography [alumina (20 × 2.7 cm)] gave the following fractions: (i) PB (4 : 1), 300 ml, orange, mixture; (ii) PB (4 : 1), 250 ml, colourless; (iii) B, 150 ml, pink followed by green (discarded); and (iv) BE (4 : 1), 200 ml, orange. Rechromatography [silica (40 × 2.0 cm)] of fraction (i) gave fractions (i) (a) PB (1 : 1), 500 ml, orange; (i) (b) PB (1 : 1), 400 ml, mixture (discarded); (i) (c) B, 100 ml, yellow, mixture; and (i) (d) BE (4 : 1), 350 ml, yellow, mixture. Fraction (i) (a) afforded the thione (25) (180 mg, 8.6%). The combined residues from fractions (i) (c) and (i) (d) were rechromatographed [alumina (50 × 2.0 cm)]. Petroleum–benzene (3 : 1) brought through yellow eluates which afforded 3-*methyl*-2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)*pyridine* (12) (399 mg, 14%), yellow needles from cyclohexane, m.p. 110—110.5 °C, *m/z* 284.0440 (M^+) (Found: C, 63.3; H, 4.2; N, 10.0. $C_{15}H_{12}N_2S_2$ requires C, 63.4; H, 4.3; N, 9.9%). Subsequent elution with benzene gave colourless eluates which, when combined with fraction (ii), gave the ketone (26) (707 mg, 36%). Rechromatography [alumina (20 × 1.5 cm)] of fraction (iv) with benzene gave orange eluates which yielded 7-*methyl*-3-*thiobenzoylmethylene*-3H-*pyrido*[2,1-c][1,2,4]*thiadiazole* (22) (24 mg, 0.8%), red prisms from benzene, m.p. 208—209 °C, *m/z* 284.0454 (M^+) (Found: C, 63.2; H, 4.0; N, 9.8. $C_{15}H_{12}N_2S_2$ requires C, 63.4; H, 4.3; N, 9.9%).

With 2-*amino*-4-*methylpyridine*. Chromatography [alumina (50 × 2.7 cm)] gave the following fractions: (i) PB (3 : 1), 100 ml, orange; (ii) PB (2 : 1), 250 ml, orange, mixture; (iii) PB (1 : 1), 400 ml, colourless; (iv) PB (1 : 1), 200 ml, red (discarded); (v) B, 600 ml, orange, mixture; and (vi) BE (3 : 1), 400 ml, orange, mixture. Fractions (i)—(iii) yielded the thione (25) (148 mg, 7%) and the ketone (26) (702 mg, 36%). Rechromatography [alumina (40 × 2.0 cm)] of fraction (v) with benzene gave orange eluates which were discarded, and then yellow eluates which

afforded 4-*methyl*-2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)-*pyridine* (13) (983 mg, 35%), yellow needles from cyclohexane, m.p. 147.5—148 °C, *m/z* 284.0451 (M^+) (Found: C, 63.2; H, 4.2; N, 9.9. $C_{15}H_{12}N_2S_2$ requires C, 63.4; H, 4.3; N, 9.9%). Fraction (vi) was rechromatographed [alumina (20 × 2.0 cm)]. Elution with benzene gave yellow eluates which were discarded. Further elution with benzene-ether (9 : 1) brought through orange eluates which yielded 6-*methyl*-3-*thiobenzoylmethylene*-3H-*pyrido*[2,1-c]-[1,2,4]*thiadiazole* (23) (18 mg, 0.6%), orange needles from benzene, m.p. 187—189 °C, *m/z* 284.0435 (M^+) (Found: C, 63.4; H, 4.2; N, 9.7. $C_{15}H_{12}N_2S_2$ requires C, 63.4; H, 4.3; N, 9.9%).

With 2-*amino*-5-*methylpyridine*. Chromatography [alumina (50 × 2.7 cm)] gave the following fractions: (i) PB (3 : 1), 600 ml, orange; (ii) PB (3 : 1), 250 ml, orange, mixture; (iii) B, 450 ml, colourless; (iv) B, 100 ml, brown (discarded); (v) BE (9 : 1), 150 ml, brown (discarded); (vi) BE (9 : 1), 500 ml, yellow, mixture; and (vii) BE (4 : 1), 300 ml, orange. Fractions (i)—(iii) yielded the thione (25) (122 mg, 5.8%) and the ketone (26) (866 mg, 44%). Rechromatography [alumina (40 × 2.0 cm)] of fraction (vi) with petroleum–benzene (2 : 1) gave fractions (vi) (a) 150 ml, brown (discarded); (vi) (b) 21, yellow; and (vi) (c) 200 ml, yellow, mixture (discarded). Fraction (vi) (b) afforded 5-*methyl*-2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)*pyridine* (14) (696 mg, 25%), yellow needles from cyclohexane, m.p. 163—164 °C, *m/z* 284.0448 (M^+) (Found: C, 63.5; H, 4.4; N, 9.9. $C_{15}H_{12}N_2S_2$ requires C, 63.4; H, 4.3; N, 9.9%). The residue from fraction (vii) was rechromatographed [alumina (20 × 1.5 cm)]. Elution with benzene gave yellow eluates which were discarded. Subsequent elution with benzene–ether (9 : 1) brought through orange eluates which yielded 5-*methyl*-3-*thiobenzoylmethylene*-3H-*pyrido*-[2,1-c][1,2,4]*thiadiazole* (24) (6 mg, 0.2%), red needles from cyclohexane–benzene, m.p. 191—192 °C, *m/z* 284.0440 (M^+) (Found: C, 63.6; H, 4.2; N, 9.8. $C_{15}H_{12}N_2S_2$ requires C, 63.4; H, 4.3; N, 9.9%).

With 2-*amino*-6-*methylpyridine*. Chromatography [alumina (50 × 2.7 cm)] gave the following fractions: (i) PB (3 : 1), 800 ml, orange; (ii) PB (3 : 1), 150 ml, orange, mixture; (iii) B, 500 ml, colourless; (iv) B, 300 ml, brown (discarded); and (v) BE (9 : 1), 550 ml, yellow, mixture. Fractions (i)—(iii) gave the thione (25) (147 mg, 7%) and the ketone (26) (477 mg, 25%). Rechromatography [alumina (40 × 2.0 cm)] of fraction (v) with petroleum–benzene (2 : 1) gave fractions (v) (a) 100 ml, brown (discarded); (v) (b) 200 ml, brown; (v) (c) 1 800 ml, yellow; and (v) (d) 200 ml, yellow changing to blue (t.l.c.). Rechromatography [alumina (40 × 2.0 cm)] of the combined residues from fractions (v) (b) and (v) (d) with petroleum–benzene (2 : 1) gave brown eluates which were discarded and subsequently yellow eluates which, when combined with fraction (v) (c), yielded 6-*methyl*-2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)-*pyridine* (15) (766 mg, 27%), yellow spars from cyclohexane, m.p. 118.5—119 °C, *m/z* 284.0432 (M^+) (Found: C, 63.2; H, 4.3; N, 9.9. $C_{15}H_{12}N_2S_2$ requires C, 63.4; H, 4.3; N, 9.9%).

With 2-*amino*-4,6-*dimethylpyridine*. Chromatography [alumina (50 × 2.7 cm)] gave the following fractions: (i) PB (3 : 1), 700 ml, orange; (ii) PB (3 : 1), 250 ml, orange, mixture; (iii) B, 400 ml, colourless; (iv) B, 100 ml, reddish brown (discarded); and (v) B, 850 ml, yellow + brown + blue components (t.l.c.). Fractions (i)—(iii) yielded the thione (25) (136 mg, 6.5%) and the ketone (26) (797 mg, 41%). The residue from fraction (v) was extracted with petroleum to remove the brown impurity and then rechromatographed [alumina (40 × 2.0 cm)] with petroleum–benzene (1 : 1). The yellow eluates afforded 4,6-*dimethyl*-2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)*pyridine* (16) (797 mg, 26%), yellow spars from cyclohexane, m.p. 120—120.5 °C, *m/z* 298.0607 (Found: C, 64.4; H, 4.4; N, 9.2. $C_{16}H_{14}N_2S_2$ requires C, 64.4; H, 4.7; N, 9.4%).

With 2-*aminopyrimidine*. Chromatography [alumina (50 × 2.7 cm)] gave the following fractions: (i) PB (3 : 1), 650 ml, orange; (ii) PB (3 : 1), 250 ml, orange, mixture; (iii) B, 700 ml, colourless; (iv) E, 500 ml and EM (19 : 1), 250 ml, blue and pink (t.l.c.) (discarded); and (v) EM (4 : 1), 500 ml, yellow. Fractions (i)—(iii) gave the thione (25) (158 mg, 7.5%) and the ketone (26) (843 mg, 43%). Rechromatography [alumina (10 × 1.5 cm)] of fraction (v) with ether–methanol (19 : 1) gave yellow eluates which yielded 2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)*pyrimidine* (17) (113 mg, 4.2%), yellow prisms from benzene–methanol, m.p. 169—171 °C, *m/z* 271.0245 (M^+) (Found: C, 57.9; H, 3.2; N, 15.7. $C_{13}H_9N_3S_2$ requires C, 57.5; H, 3.3; N, 15.5%).

With 2-*aminobenzimidazole*. A solution of the reaction products in warm benzene (700 ml) was passed down a column of alumina (15 × 2.0 cm), and elution was continued with benzene until 1 l of orange and then 1 l of colourless eluate had been collected. Further elution gave successively brown eluates [BE (1 : 1), 200 ml; E, 200 ml] which were discarded, and orange-yellow eluates [EM (99 : 1), 250 ml]. The benzene eluates yielded the thione (25) (225 mg, 10.1%) and the ketone (26) (786 mg, 40%). The residue from the orange-yellow eluates was dissolved in boiling acetone, hot benzene was added, and solvent was boiled off to the point of incipient crystallisation. The cooled solution gave 2-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)*benzimidazole* (18) (108 mg, 3.5%), orange prisms, m.p. 288—290 °C (sublimation >230 °C), *m/z* 309.0380 (M^+) (Found: C, 61.9; H, 3.6; N, 13.5. $C_{16}H_{11}N_3S_2$ requires C, 62.1; H, 3.6; N, 13.6%).

With 2,6-*diaminopyridine*. Chromatography [alumina (20 × 2.7 cm)] gave the following fractions: (i) B, 300 ml, orange, mixture; (ii) BE (9 : 1), 400 ml, yellow ⟶ orange, mixture; and (iii) EM (4 : 1), 750 ml, pink. Fraction (i) yielded the thione (25) (296 mg, 14.1%) and the ketone (26) (170 mg, 8.8%). Rechromatography [alumina (50 × 2.0 cm)] of fraction (ii) with benzene–ether (9 : 1) gave orange eluates (1 l) which yielded 2,6-*bis*-(5-*phenyl*-1,2-*dithiol*-3-*ylideneamino*)*pyridine* (52) (181 mg, 7.9%), orange plates from benzene, m.p. 191—192 °C, *m/z* 461.0118 (M^+) (Found: C, 59.8; H, 3.4; N, 9.1. $C_{23}H_{15}N_3S_4$ requires C, 59.8; H, 3.3; N, 9.1%). Rechromatography [alumina (15 × 3.5 cm)] of fraction (iii) with ether–methanol (5 : 2) gave pink eluates which afforded 4-(5-*phenyl*-1,2-*dithiol*-3-*ylidenamino*)-3-*thiobenzoylmethylene*-3H-*pyrido*[2,1-c][1,2,4]-*thiadiazole* (53) (136 mg, 5.9%), red rods from benzene, m.p. 286—288 °C, *m/z* 461.0129 (Found: C, 60.1; H, 3.0; N, 8.8. $C_{23}H_{15}N_3S_4$ requires C, 59.8; H, 3.3; N, 9.1%).

Condensation of 3-*Methoxy*-5-*phenyl*-1,2-*dithiolylium Fluorosulphonate* (7) *with* 2-*Amino*-N-*heterocycles in Ethanol*. —The procedure was identical with that for the reactions of the salt (6) with 2-amino-*N*-heterocycles, with 3-methoxy-5-phenyl-1,2-dithiolylium fluorosulphonate (7) (10 mmol) in place of the salt (6).

With 2-*amino*-Δ^2-*thiazoline*. Chromatography [alumina (50 × 2.7 cm)] gave the following fractions: (i) PB (3 : 1), 100 ml, purple (discarded); (ii) PB (3 : 1), 400 ml, orange;

(iii) PB (2 : 1), 250 ml, orange, mixture; (iv) PB (1 : 1), colourless; (v) B, 750 ml; BE (9 : 1), 300 ml (discarded); and (vi) BE (9 : 1), 800 ml, orange. Fractions (ii)—(iv) gave the thione (25) (293 mg, 13.9%) and the ketone (26) (359 mg, 18.5%). Rechromatography [alumina (30 × 2.0 cm)] of fraction (vi) with benzene–ether (9 : 1) gave successively non-homogeneous orange eluates (100 ml) which were discarded, and orange eluates (1 l) which yielded 4,5-dihydro-3-thiobenzoylmethylene-3*H*-thiazolo[2,3-*c*][1,2,4]-thiadiazole (19) (278 mg, 10.3%).

With 2-aminothiazole. Chromatography was carried out with silica (50 × 2.0 cm). Elution with petroleum–benzene (1 : 1) gave yellow eluates which afforded the thione (25) (308 mg, 14.6%). Further elution with benzene gave three-component eluates (100 ml) which were discarded, and non-homogeneous yellow eluates (500 ml), the residue from which was rechromatographed [alumina (40 × 2.0 cm)]. Elution with petroleum–benzene (3 : 1) (350 ml) gave yellow eluates, which contained a small quantity of the ketone (26) and compound (10), and were discarded. Continued elution with petroleum–benzene [3 : 1, 350 ml; 1 : 1, 750 ml] brought through yellow eluates which yielded 2-(5-phenyl-1,2-dithiol-3-ylideneamino)thiazole (10) (464 mg, 16.8%).

With 2-amino-4-methylpyridine. The chromatographic procedure followed closely the procedure used to separate the products of the reaction of the salt (6) with 2-amino-4-methylpyridine in ethanol and gave the thione (25) (518 mg, 25%), the ketone (26) (481 mg, 25%), and 4-methyl-2-(5-phenyl-1,2-dithiol-3-ylideneamino)pyridine (13) (420 mg, 14.8%). Compound (23) was not detected.

Condensation of 3-Chloro-5-phenyl-1,2-dithiolylium Chloride (6) *with 2-Amino-Δ²-thiazoline in Acetonitrile.*—The procedure was identical with that for the reaction of the salt (6) with 2-amino-Δ²-thiazoline in ethanol, with acetonitrile (60 ml) in place of ethanol. Chromatography [alumina; activity II, pH *ca.* 9.5, 100—200 mesh (50 × 2.7 cm)] gave the following fractions: (i) B, 500 ml, orange; (ii) BE (4 : 1), 500 ml, orange; (iii) BE (1 : 1), 300 ml, colourless; (iv) E, 600 ml, yellow; and (v) EM (9 : 1), 200 ml, orange, mixture. Fractions (i) and (ii) gave the thione (25) (505 mg, 24%). Fraction (iii) contained a small amount of the ketone (26) and was discarded. Rechromatography [silica (30 × 1.8 cm)] of fraction (iv) gave successively yellow eluates (B, 950 ml) which were discarded, and homogeneous yellow eluates [BE (9 : 1), 500 ml; BE (4 : 1), 500 ml; BE (1 : 1), 500 ml] which yielded 4,5-dihydro-2-(5-phenyl-1,2-dithiol-3-ylideneamino)thiazole (9) (289 mg, 10.4%). A small amount (t.l.c.) of compound (19) in fraction (v) could not be obtained pure.

Synthesis of 6-Methyl-3-thiobenzoylmethylene-3H-pyrido-[2,1-c][1,2,4]thiadiazole (23) *from 4-methyl-2-trichloromethylthioaminopyridine.—Preparation of 4-methyl-2-trichloromethylthioaminopyridine* (28). The procedure was a modification of the method of Goerdeler and Erbach.[4] Solutions of 2-amino-4-methylpyridine (10.81 g, 100 mmol) in ether (150 ml), trichloromethanesulphenyl chloride (18.57 g, 10.95 ml, 100 mmol) in ether (60 ml), and sodium carbonate (10.60 g, 100 mmol) in water (100 ml) were added simultaneously during 1 h to ether (600 ml). A little of the trichloromethanesulphenyl chloride solution was added first, and the reaction mixture was stirred vigorously and kept at *ca.* 0 °C during the addition. After the addition was complete, the ether layer was washed with water (× 4) and dried, and the solvent was evaporated off on a cold water-bath. The residual solid was washed with petroleum and recrystallised from ether. *4-Methyl-2-trichloromethylthioaminopyridine* (12.55 g, 49%) was obtained as rods, m.p. 118.5—120 °C (decomp.) (Found: C, 32.5; H, 2.6; N, 10.7. $C_7H_7Cl_3N_2S$ requires C, 32.6; H, 2.7; N, 10.9%); *m/z* 255.9406 (M^+); δ 2.33 (3 H, br, 4-Me), 6.72 (1 H, d, $J_{5,6}$ 5.0 Hz, 5-H), 7.25 (1 H, br, 3-H), and 8.08 (1 H, d, $J_{6,5}$ 5.0 Hz, 6-H).

Condensation of 4-methyl-2-trichloromethylthioaminopyridine (28) *with benzoylacetic acid.* (*a*) The sulphenamide (28) (6.44 g, 25 mmol) was added with dimethylformamide (50 ml) to a stirred, freshly prepared solution of benzoylacetic acid (4.11 g, 25 mmol) and triethylamine (15.18 g, 20.85 ml, 150 mmol) in dimethylformamide (200 ml) at room temperature. The resulting mixture was stirred for 1 h, poured into water, and extracted with benzene (× 2). The extracts were washed with water (× 6), dried, and evaporated. Chromatography [alumina (30 × 2.7 cm)] of the residue gave the following fractions: (i) B, 650 ml, pale yellow, three-component mixture; (ii) BE (4 : 1), 300 ml, yellow (discarded); (iii) E, 800 ml, yellow. Rechromatography [alumina (60 × 2.7 cm)] of fraction (i) gave successively yellow eluates [PB (1 : 1), 250 ml)] which contained (t.l.c.) acetophenone and compound (31) and were discarded, and colourless eluates [PB (1 : 1, 250 ml; PB (1 : 2), 300 ml; B, 900 ml] which yielded *6-methyl-3H-pyrido[2,1-c][1,2,4]-thiadiazol-3-one* (32) (2.02 g, 49%), spars from cyclohexane, m.p. 124—125.5 °C (Found: C, 50.8; H, 3.4; N, 17.0. $C_7H_6N_2OS$ requires C, 50.6; H, 3.6; N, 16.9%); *m/z* 166.0203 (M^+); δ 2.30 (3 H, d, $J_{6\text{-Me},7}$ 1.4 Hz, 6-Me), 6.40 (1 H, dd, $J_{5,4}$ 7.2, $J_{5,7}$ 1.6 Hz, 5-H), 6.87 (1 H, m, $J_{7,5}$ 1.6, $J_{7,6\text{-Me}}$ 1.4 Hz, 7-H), and 7.71 [1 H, d (further split), br, $J_{4,5}$ 7.2 Hz, 4-H]. Rechromatography [alumina (20 × 2.7 cm)] of fraction (iii) with ether gave yellow eluates which afforded *6-methyl-3-benzoylmethylene-3H-pyrido[2,1-c][1,2,4]thiadiazole* (30) (551 mg, 8.2%), yellow plates from benzene, m.p. 240—241 °C, *m/z* 268.0657 (M^+) (Found: C, 67.1; H, 4.4; N, 10.4. $C_{15}H_{12}N_2OS$ requires C, 67.1; H, 4.5; N, 10.4%).

(*b*) Benzoylacetic acid (824 mg, 5 mmol) was dissolved in a small volume of water containing sodium hydroxide (200 mg, 5 mmol), and the solution was added to a solution of the sulphenamide (28) (1.288 g, 5 mmol) in ethanol (100 ml) containing an excess of sodium carbonate in suspension. The resulting yellow mixture was stirred for 24 h, diluted with water, and extracted with benzene. The extracts were washed with water (×3), dried, and evaporated, and the residue was chromatographed [alumina (40 × 2.0 cm)]. Elution with benzene gave yellow eluates which afforded 6-methyl-3-(4-methyl-2-pyridylimino)-3*H*-pyrido[2,1-*c*]-[1,2,4]thiadiazole (31) (487 mg, 76%), yellow prisms from cyclohexane, m.p. 192.5—194 °C, mixed m.p. with an authentic sample purified by chromatography 192—194 °C (lit.,[9] orange needles, m.p. 189—192 °C) (Found: C, 61.0; H, 4.6; N, 22.2. Calc. for $C_{13}H_{12}N_4S$: C, 60.9; H, 4.7; N, 22.9%). Continued elution with benzene–ether (9 : 1 ⟶ 4 : 1) brought through yellow eluates, the residue from which was rechromatographed [alumina (10 × 1.5 cm)] with benzene–ether (1 : 1). The yellow eluates yielded 6-methyl-3-benzoylmethylene-3*H*-pyrido[2,1-*c*][1,2,4]thiadiazole (30) (13 mg, 0.97%).

Thionation of 6-Methyl-3-benzoylmethylene-3H-pyrido[2,1-c][1,2,4]thiadiazole (30). (*a*) Tetraphosphorus decasulphide (444 mg, 1 mmol) was added with pyridine (5 ml) to a solution of compound (30) (268 mg, 1 mmol) in pyridine (20 ml), and the resulting mixture was boiled for 1 h. The cooled mixture was poured into water and extracted with benzene

(× 3), and the extracts were washed with water (× 3), dried, and evaporated. Chromatography [alumina (25 × 2.0 cm)] of the residue with benzene gave yellow eluates which afforded the thione (25) (10 mg, 4.8%). Subsequent elution with benzene–ether (3 : 1) brought through orange eluates which yielded 6-methyl-3-thiobenzoylmethylene-3*H*-pyrido-[2,1-*c*][1,2,4]thiadiazole (23) (41 mg, 14.4%). Elution finally with ether–methanol (99 : 1) gave yellow eluates from which starting material (172 mg, 64%) was recovered.

(*b*) Tetraphosphorus decasulphide (667 mg, 1.5 mmol) was added to a solution of compound (30) (268 mg, 1 mmol) in toluene (25 ml), and the mixture was boiled for 1 h. The cooled mixture was poured into water, the resulting mixture was extracted with benzene (× 3), and the residue from the dried and evaporated extracts was chromatographed [alumina (20 × 1.8 cm)]. Elution with petroleum–benzene (1 : 1) gave yellow eluates which afforded the thione (25) (137 mg, 65%). Continued elution with benzene–ether (1 : 2) gave orange eluates which yielded compound (23) (2 mg) (identified by comparative t.l.c.). Subsequent elution with ether brought through yellow eluates from which starting material (21 mg, 7.8%) was recovered.

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