Novel Heteropentalenes. Synthesis of the Nabam Oxidation Product and Related Compounds

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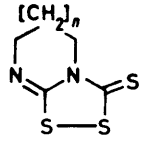
5,6-Dihydroimidazo[2,1-*c*][1,2,4]dithiazole-3-thione [the oxidation product of disodium ethylenebis(dithiocarbamate)] and analogues containing reduced pyrimidine and benzimidazole rings have been synthesised by the action of carbon disulphide on (benzylthio)isothiourea and phenacylisothiourea derivatives of cyclic thioureas. Similar reactions with phenyl isothiocyanate and other heterocumulenes lead to the novel heteropentalenes, 2,3,4,5-tetrahydro-2,5-bis(phenylimino)-3,4-ethano-1,6,6aλ^4-trithia-3,4-diazapentalene, 2,3,4,5-tetrahydro-1,6-diphenyl-3,4-propano-6aλ^4-thia-1,3,4,6-tetra-azapentalene-2,5-dithione, the corresponding 2,5-dione, and 2,3,4,5-tetrahydro-1,6-dimethyl-3,4-propano-6aλ^4-thia-1,3,4,6-tetra-azapentalene-2,5-dithione.

THE antifungal compound obtained by autoxidation of disodium ethylenebis(dithiocarbamate) (Nabam), originally thought to be ethylenethiuram monosulphide (E.T.M.), was reformulated [1] in 1971 as the imidazodithiazole (1). The revised structure was subsequently supported by ^{13}C n.m.r. studies and by the observation that electrochemical reduction of the oxidation product generates ethylenethiourea (2-imidazolidinethione).[2]



(1) $n = 0$
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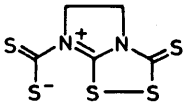


(3)

Our interest was stimulated by the report that this compound readily forms a carbon disulphide adduct, formulated as (3), and by the suggestion that the adduct may be structurally related to the heteropentalenes.[3,4] As a result, we initiated an investigation which had two objectives: first, to devise rational syntheses of the imidazodithiazole (1) and analogues [*e.g.* (2)], and second, to study addition reactions of these compounds with heterocumulenes.[5]

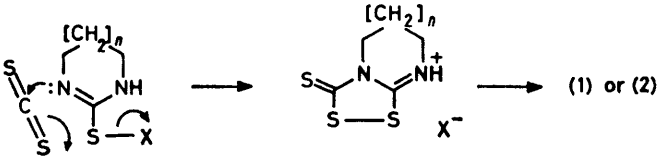
RESULTS AND DISCUSSION

The synthetic route envisaged is summarised in Scheme 1; conversion of a cyclic thiourea to an isothiourea derivative produces a nucleophilic centre at one of the nitrogen atoms, which should add to the electrophilic carbon of carbon disulphide, generating in turn a nucleophilic centre on sulphur. Formation of the disulphide link should then follow, provided that X can function as a leaving group.

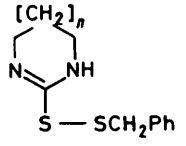
After some preliminary experimentation, it was found that the predicted reactions occur satisfactorily with the *S*-(benzylthio)isothiourea (4) derived from ethylenethiourea and prepared by the method described by Sirakawa *et al.*[6] for *S*-(benzylthio)isothiourea. Treatment of the hydrochloride of compound (4) with carbon disulphide in the presence of sodium hydrogencarbonate gave the red, insoluble, adduct (3) which is thermally unstable and readily reverts to the imidazodithiazole (1).

A less direct route involved, as a first step, treatment of the hydrochloride of the isothiourea (4) with phenyl isothiocyanate and sodium hydrogencarbonate which, according to Scheme 1, might have led to the imidazodithiazole (6) or to the isomeric imidazothiadiazole (7). Analysis of the yellow product indicated that two molecules of phenyl isothiocyanate had been added. The symmetrical heteropentalene structure (8) was assigned to this product on the basis of spectroscopic evidence, and a crystallographic study [7] subsequently showed that the structural assignment was correct.

When the phenyl isothiocyanate adduct was heated with carbon disulphide, the isothiocyanate residues were displaced and the adduct (3) was isolated from the cooled reaction mixture. Conversely, when the imidazodithiazole (1) was treated with phenyl isothiocyanate at room temperature, the heteropentalene (8) was formed, presumably by one of the routes shown in Scheme 2.



SCHEME 1



(4) $n = 0$
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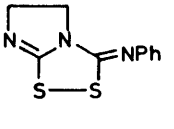
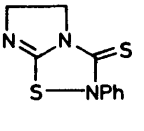
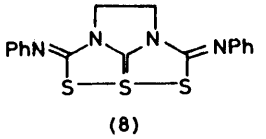


(6)

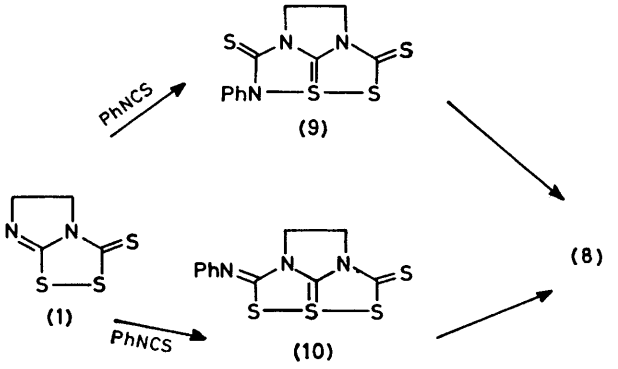


(7)



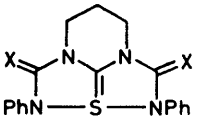
(8)

Attempts to isolate the postulated intermediates (9) or (10) were unsuccessful. Phenyl isocyanate also reacts with the imidazodithiazole but the adduct dissociates in solution.

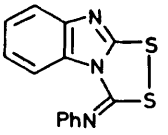


SCHEME 2

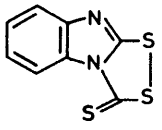
The synthetic procedure (Scheme 1) has been applied to the preparation of the homologous dithiazole (2). Interestingly, this product does not add carbon disulphide under conditions which, in the case of the imidazodithiazole, readily lead to an adduct. It does, however, react with phenyl isothiocyanate, adding two molecules and yielding a well-defined product which, from the n.m.r. data, has a symmetrical structure. Unlike the heteropentalene (8), this compound is colourless and we therefore formulate it as the heteropentalene (11). A similar structure (12) is assigned to the product obtained from the dithiazole (2) and phenyl isocyanate. Here, the structure assignment is unambiguous, because the i.r. spectrum contains a strong (and broad) C=O stretching absorption band.



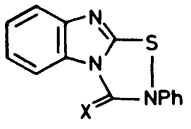
(11) X = S
(12) X = O



(13)



(14)

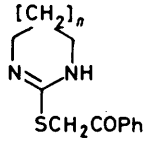


(15) X = S
(16) X = O

Extension of the method into the benzimidazole series has afforded the four compounds (13), (14), (15), and (16). 2-Benzimidazolyl benzyl disulphide and phenyl isothiocyanate, when heated together, gave the yellow phenyliminobenzimidazodithiazole (13). The failure of this product to add a second molecule of phenyl isothiocyanate is noteworthy. Prolonged heating with carbon disulphide converted compound (13) to the benzimidazolethione (14), analogous to the Nabam oxidation product. Again, there was no indication of addition of a second molecule of heterocumulene. Treatment of the benzimidazodithiazolethione (14) with phenyl isothiocyanate regenerated the phenylimine (13).

A colourless isomer (15) of compound (13) was formed when bis(2-benzimidazolyl) disulphide was heated with phenyl isothiocyanate; a higher temperature was required than for the reaction leading to (13). The assignment of structure (15) is supported by the conversion to the thiadiazolone (16) with mercuric acetate in hot acetic acid.

The synthetic approach of Scheme 1 clearly has some generality when the leaving group X is a thiolate anion. In a later development of our work, it was found that *S*-phenacyl derivatives of cyclic thioureas could also function satisfactorily as substrates for attack by heterocumulenes (X = CH_2COPh in Scheme 1).



(17) *n* = 0
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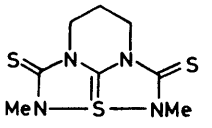


(19)

Thus, 2-(phenacylthio)-1-imidazoline (17), when heated with carbon disulphide, gives the carbon disulphide adduct (3) of the Nabam oxidation product; with phenyl isothiocyanate, the heteropentalene (8) is produced in 89% yield, the eliminated phenacyl group appearing as acetophenone which was isolated as its 2,4-dinitrophenylhydrazone. Similarly, 2-(phenacylthio)-3,4,5,6-tetrahydropyrimidine (18) was converted to the dithiazole (2), to the heteropentalenes (11) and (12), and also to the *NN'*-dimethyl compound (19), a member of the series not made in the earlier work.

It seems unlikely that, in these reactions, the phenacyl residue could be expelled as a carbanion. Scheme 3 illustrates two possible ways in which the attack by the heterocumulene could bring about the loss of the enolic form of acetophenone, taking account of the equilibrium between the keto- and cyclised carbinolamine forms of *S*-phenacylisothioureas.[8,9]

The structures of the heteropentalenes (8), (11), (12), and (19) deserve comment. They are well-defined, stable compounds; two of them, (8) and (11), can be sublimed with little decomposition. The n.m.r. data indicate that, in solution, their structures have real or time-averaged symmetry. But, unlike the heteropentalenes of the thiathiophthen type, of which many examples are now known,[4] these compounds can hardly be regarded as aromatic. They are effectively tetrahydroheteropentalene derivatives, and the distribution of bond lengths in compound (8),[7] especially in the N–C–N–C–N–C–N sequence, eliminates any possibility of a highly polarised structure which might be considered to have aromatic stabilisation. In the absence

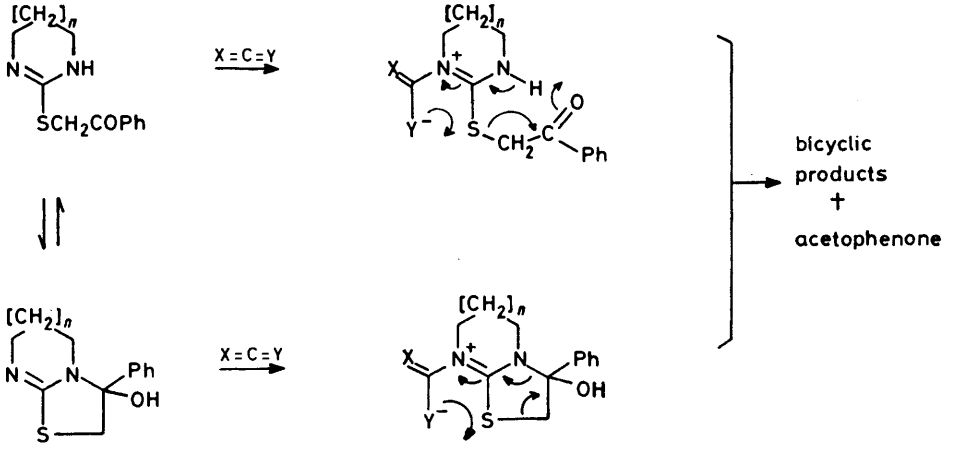
of such stabilisation, the four heteropentalenes should perhaps be regarded as compounds with particularly favourable electron-rich three-centre bonds.

If this assumption is made, several problems remain. One of these concerns the nature of the carbon disulphide adduct (3), which is clearly different in character from the heteropentalenes discussed above. It is thermally unstable and extremely insoluble in most solvents at room temperature; it dissolved in dimethyl sulphoxide, but some dissociation is indicated by the n.m.r. data.[1]

A second problem is posed by the different effects of the ethano- and propano-bridges linking the nitrogen atoms at positions 3 and 4 of the reduced heteropentalene systems. The arrangement in structure (8) must be energetically preferable to the alternative dithione structure with a linear N–S–N system. Compounds (11) and (19), with the propano-bridge, prefer the dithione structures.

A possible explanation is that the ethano-bridge introduces some strain into the heteropentalene molecule with the linear N–S–N system; this strain might be absent with the longer S–S–S linkage. With the propano-bridge, strain might be produced with the S–S–S arrangement, but relieved by the shorter N–S–N system. In the benzimidazole series, the fusion of the benzene and the imidazole rings presumably introduces so much strain into the heteropentalene system that it does not form, although here a change in character of the nitrogen atoms might well be important.

It is clear that further studies of heteropentalenes of this novel type are desirable.



SCHEME 3

EXPERIMENTAL

M.p.s were determined on a Kofler hot stage apparatus. Light petroleum refers to the fraction of b.p. 60—80 °C.

2-(4,5-*Dihydroimidazolyl*) *Benzyl Disulphide* (4).—A mixture of imidazolidine-2-thione (10.8 g), phenylmethanethiol (11 g), ethanol (350 ml), concentrated hydrochloric acid (14 ml), and water (14 ml) was cooled to 0 °C (ice–salt-bath) and stirred over a period of 1 h whilst a solution of hydrogen peroxide (11.2 g, of 27.5% aqueous solution) in ethanol (25 ml) was added. After being stirred at 0—10 °C for a further 2 h, the mixture was filtered, and the filtrate concentrated under reduced pressure (safety screen). The oily residue was redissolved in the minimum quantity of absolute ethanol, and ether was added to precipitate the product, which was collected after 16 h at 0 °C. The colourless crystalline *hydrochloride* of 2-(4,5-*dihydroimidazolyl*) *benzyl disulphide* had no distinct m.p.; δ(D_2O) 7.58 (5 H, s), 4.20 (2 H, s), and 3.70 (4 H, s) (Found: C, 42.5; H, 5.3; N, 10.1; S, 23.0. $C_{10}H_{13}N_2S_2Cl{\cdot}H_2O$ requires C, 43.0; H, 5.4; N, 10.1; S, 23.0%). This product (0.65 g) and benzimidazoline-2-thione (0.35 g) in methanol (15 ml), treated with a solution of sodium hydrogencarbonate (0.3 g) in water (12 ml) for 30 min, gave a precipitate of 2-benzimidazolyl benzyl disulphide (0.4 g), m.p. 141—142 °C (lit.,[6] 143—144 °C), identical with an authentic sample.

5,6-*Dihydroimidazo*[2,1-c][1,2,4]*dithiazole*-3-*thione* (1).—The hydrochloride of the dihydroimidazolyl benzyl disulphide (2 g) and carbon disulphide (30 ml) were stirred vigorously with a solution of sodium hydrogencarbonate (0.66 g) in water (25 ml) for 5 h. The product was extracted with warm chloroform and the resulting solution concentrated to small volume at atmospheric pressure. After purification by chromatography on silica gel, using chloroform–ethyl acetate (1 : 1) to elute the product, the dithiazole was obtained as pale yellow needles (0.41 g), m.p. 125 °C (lit.,[10] 125 °C) from chloroform–ethyl acetate; δ($CDCl_3$) 3.87 (2 H, t) and 4.47 (2 H, t); $\lambda_{max.}$(EtOH) 225 and 280 nm (ε 8 900 and 18 000); *m/e* 176 (M^+) (Found: C, 27.5; H, 2.3; N, 15.8. Calc. for $C_4H_4N_2S_3$: C, 27.3; H, 2.3; N, 15.9%). The product was identical with a sample obtained by autoxidation of disodium ethylenebis(dithiocarbamate).

2,3,4,5-*Tetrahydro*-2,5-*bis*(*phenylimino*)-3,4-*ethano*-1,6,6aλ^4-*trithia*-3,4-*diazapentalene* (8).—Sodium hydrogencarbonate (0.32 g) in water (20 ml) was added to a solution of 2-(4,5-dihydroimidazolyl) benzyl disulphide hydrochloride (1 g) and phenyl isothiocyanate (0.6 ml) in methanol (50 ml), and the mixture was stirred for 30 min. The supernatant liquid was decanted off and the oily product was solidified with light petroleum. A further small quantity of the product was obtained by chloroform extraction of the reaction mixture. The *trithiadiazapentalene* crystallised from benzene–light petroleum as yellow needles (0.3 g), m.p. 163 °C; $\lambda_{max.}$(CH_2Cl_2) 259 and 309 nm (ε 44 400 and 16 400); δ($CDCl_3$) 6.80—7.40 (10 H,

m) and 4.60 (4 H, s) (Found: C, 54.9; H, 3.9; N, 15.3. $C_{17}H_{14}N_4S_3$ requires C, 55.1; H, 3.8; N, 15.1%).

The same product (0.17 g) was obtained when a solution of 5,6-dihydroimidazo[2,1-*c*][1,2,4]dithiazole-3-thione (0.1 g) and phenyl isothiocyanate (0.3 ml) in benzene (10 ml) was set aside for 18 h at room temperature. The reverse reaction was accomplished by heating the trithiadiazapentalène (1 g) with carbon disulphide (80 ml) containing sulphur (1 g) for 18 h. The carbon disulphide addition product of the dithiazolethione (0.45 g), which separated on cooling, was heated in benzene for 30 min. After purification by chromatography on silica in chloroform, the resulting dithiazolethione was obtained as yellow needles (0.17 g), m.p. 124—126 °C, identical with the sample previously obtained.

Reactions of 5,6-*Dihydroimidazo*[2,1-c][1,2,4]*dithiazole*-3-*thione* (1).—When heated under reflux in benzene (15 ml) for 16 h with dimethyl sulphate (0.3 ml), the dithiazolethione (0.2 g) formed a highly insoluble yellow *methosulphate* (0.14 g), m.p. 118—120 °C (Found: C, 23.8; H, 3.4; N, 9.1. $C_6H_{10}N_2O_4S_4$ requires C, 23.8; H, 3.3; N, 9.3%).

With phenyl isocyanate (0.25 g) in benzene (13 ml) the dithiazolethione (0.1 g) formed an unstable polar adduct (0.14 g), m.p. 95 °C. Attempts to obtain spectroscopic data on this product indicated that it dissociated in solution.

The dithiazolethione slowly decomposed when heated with mercuric acetate in acetic acid but the only pure material isolated after chromatography was the original thione.

5,6-*Dihydropyrimido*[2,1-c][1,2,4]*dithiazole*-3(7H)-*thione* (2).—Concentrated hydrochloric acid (7 ml), diluted with water (7 ml), was added to hexahydropyrimidine-2-thione (6.14 g) [11] and phenylmethanethiol (5.5 g) in ethanol (300 ml). The mixture was cooled to 0 °C with stirring, and hydrogen peroxide (5.6 g of 27% solution) was added gradually over 45 min, the temperature being maintained between 0 and 5 °C both during the addition, and for a further 3 h. The solution was then concentrated under reduced pressure (safety screen) and the residual oil [containing the hydrochloride of 2-(3,4,5,6-tetrahydropyrimidyl) benzyl disulphide] was dissolved in the minimum amount of dry ethanol; after addition of ether, the solution was set aside overnight at 0 °C. The oil which separated, and which could not be crystallised, was suspended in carbon disulphide (50 ml) with vigorous stirring. A solution of sodium hydrogencarbonate (3.4 g) in water (50 ml) was added during 5 min, and the resulting mixture stirred for 2 h. Extraction with chloroform (3 × 50 ml) gave 5,6-*dihydropyrimido*[2,1-c][1,2,4]*dithiazole*-3(7H)-*thione* as yellow needles (1.0 g), m.p. 154—156 °C; $\lambda_{max.}(CH_2Cl_2)$ 274 nm (ε 21 200); δ($CDCl_3$) 1.95 (2 H, m), 3.58 (2 H, t), and 4.08 (2 H, t); *m/e* 190 (M^+) (Found: C, 31.8; H, 3.4; N, 14.5. $C_5H_6N_2S_3$ requires C, 31.6; H, 3.2; N, 14.7%).

2,3,4,5-*Tetrahydro*-1,6-*diphenyl*-3,4-*propano*-6aλ⁴-*thia*-1,3,4,6-*tetra-azapentalene*-2,5-*dithione* (11).—The foregoing pyrimidodithiazole-thione (0.2 g) was mixed with phenyl isothiocyanate (2 ml) in benzene (10 ml). After 2 h at room temperature, the benzene was removed under reduced pressure and the semi-solid residue was triturated with light petroleum. The resulting solid was purified by chromatography on silica in chloroform; elution with chloroform–ethyl acetate (95 : 5) gave the 6a-*thia*-1,3,4,6-*tetra-azapentalene*-2,5-*dithione* as colourless needles (0.36 g), from ethanol, m.p. 179—180 °C; $\lambda_{max.}$(EtOH) 219 and 267 nm (ε 33 600 and 24 700); δ($CDCl_3$) 2.45 (2 H, m), 4.50 (4 H, t), and 7.37 (10 H, s) (Found: C, 56.0; H, 4.0; N, 14.9. $C_{18}H_{16}N_4S_3$ requires C, 56.3; H, 4.2; N, 14.6%).

The same product was obtained when the hydrochloride of the tetrahydropyrimidyl benzyl disulphide (12 g of the crude material prepared as described above), dissolved in methanol (50 ml) containing phenyl isothiocyanate (2 ml), was treated with sodium hydrogencarbonate (5 g) in water (20 ml), with vigorous stirring. Extraction with methylene chloride, trituration of the product with light petroleum, and crystallisation from ethanol gave the pure thiatetra-azapentalene as colourless needles (7.8 g), m.p. 178—180 °C.

2,3,4,5-*Tetrahydro*-1,6-*diphenyl*-3,4-*propano*-6aλ⁴-*thia*-1,3,4,6-*tetra-azapentalene*-2,5-*dione* (12).—A solution of 5,6-dihydropyrimido[2,1-*c*][1,2,4]dithiazole-3(7*H*)-thione (0.052 g) and phenyl isocyanate (0.1 g) in benzene was set aside at room temperature for 16 h. Evaporation of the solvent gave the *thiatetra-azapentalene*-2,5-*dione* which crystallised from benzene as colourless needles (0.085 g), m.p. 210—212 °C; $\nu_{max.}$ 1 690—1 710 cm^{-1}; $\lambda_{max.}$(EtOH) 235 and 263 nm (ε 20 400 and 12 100); δ($CDCl_3$) 2.10 (2 H, m), 3.85 (4 H, t), and 6.90—7.40 (10 H, m) (Found: C, 61.4; H, 4.7; N, 16.0; S, 9.3. $C_{18}H_{16}N_4O_2S$ requires C, 61.4; H, 4.6; N, 15.9; S, 9.1%).

3-(*Phenylimino*)*benzimidazo*[2,1-c][1,2,4]*dithiazole* (13).—An intimate mixture of 2-benzimidazolyl benzyl disulphide (1 g) [6] and phenyl isothiocyanate (3 ml) was heated, under nitrogen, to 110 °C for 1 h. Methylene chloride (15 ml) was added to the cooled mixture and insoluble material (benzimidazoline-2-thione) removed by filtration. After purification by chromatography on silica in methylene chloride, the *benzimidazodithiazole* was obtained as pale yellow needles (0.38 g), m.p. 152—153 °C, from ethanol; $\lambda_{max.}(CH_2Cl_2)$ 244, 250, and 274 nm (ε 25 200, 25 200, and 15 500); *m/e* 283 (M^+) (Found: C, 59.1; H, 3.3; N, 14.6. $C_{14}H_9N_3S_2$ requires C, 59.4; H, 3.2; N, 14.8%).

Benzimidazo[2,1-c][1,2,4]*dithiazole*-3-*thione* (14).—3-(Phenylimino)benzimidazo[2,1-*c*][1,2,4]dithiazole (0.35 g) was heated under reflux with carbon disulphide (25 ml) containing sulphur (0.35 g) for 24 h. The resulting solid was purified by chromatography on silica in methylene chloride; the *benzimidazodithiazolethione* crystallised from toluene in yellow needles (0.18 g), m.p. 192—194 °C; $\lambda_{max.}(CH_2Cl_2)$ 269, 305, and 358 nm (ε 35 100, 10 200, and 4 720); *m/e* 224 (M^+) (Found: C, 42.6; H, 1.8; N, 12.3. $C_8H_4N_2S_3$ requires C, 42.9; H, 1.8; N, 12.5%).

This product (0.03 g) and phenyl isothiocyanate (0.2 ml) in toluene (10 ml) were heated under reflux for 2 h. The oil left after removal of toluene crystallised on treatment with light petroleum; recrystallisation from ethanol gave 3-phenyliminobenzimidazo[2,1-*c*][1,2,4]dithiazole (0.018 g), m.p. 152—154 °C.

2-*Phenylbenzimidazo*[2,1-b][1,2,4]*thiadiazole*-3-*thione* (15).—Bis(2-benzimidazolyl) disulphide (1 g) [12] and phenyl isothiocyanate (2 ml) were mixed and heated to 180—200 °C for 1 h. The resulting mixture was heated with ethanol (50 ml) for 15 min to remove soluble impurities, and the solid obtained by filtration was then crystallised from tetrahydrofuran giving the *thione* as colourless needles (0.54 g), m.p. 341—342 °C; $\lambda_{max.}$(EtOH) 278, 285, 317, and 325 nm (ε 24 400, 24 400, 16 600, and 15 600); *m/e* 283 (M^+) (Found: C, 59.3; H, 3.3; N, 14.3; S, 22.5. $C_{14}H_9N_3S_2$ requires C, 59.4; H, 3.2; N, 14.8; S, 22.6%).

The thione (1 g), heated with mercury(II) acetate (2.24 g) in acetic acid for 4 h gave, after filtration and evaporation of solvent, an oily product which solidified on treatment

with methylene chloride; crystallisation from aqueous ethanol yielded colourless microcrystals of 2-*phenylbenzimidazo*[2,1-b][1,2,4]*thiadiazole*-3-*one* (0.23 g), m.p. 273—274 °C; $\nu_{max.}$ 1 725 cm^{-1}; $\lambda_{max.}$(EtOH) 227, 281, 290, and 301 nm (ε 34 500, 27 200, 21 800, and 19 700); *m/e* 267 (M^+).

Reactions of 2-(*Phenacylthio*)-2-*imidazoline* (17).—2-(Phenacylthio)-2-imidazoline [9] (1.5 g) was heated under reflux with carbon disulphide (50 ml) for 7 h. The filtered reaction mixture gave a red solid on cooling. Extraction with warm chloroform and purification by chromatography on silica using chloroform–ethyl acetate (1 : 1) as eluant gave 5,6-dihydroimidazo[2,1-*c*][1,2,4]dithiazole-3-thione (0.3 g), m.p. 123 °C, identical with the sample described previously.

A mixture of the (phenacylthio)imidazoline (1 g) and phenyl isothiocyanate (2 g) was stirred and maintained at 80—90 °C for 1 h. The crude product was triturated with a little light petroleum, and the resulting yellow solid crystallised from benzene–light petroleum, giving 3,4-ethano-2,3,4,5-tetrahydro-2,5-bis(phenylimino)-1,6,6aλ⁴-trithia-3,4-diazapentalene (1.5 g), m.p. 163 °C, identical with an authentic sample (Found: C, 54.9; H, 3.8; N, 15.0%).

In a parallel experiment, the crude product was washed with ethanol and the filtered solution treated with an ethanolic solution of 2,4-dinitrophenylhydrazine hydrochloride. The expected derivative, acetophenone 2,4-dinitrophenylhydrazone, m.p. 246 °C, was obtained in 40% yield.

Reactions of 2-(*Phenacylthio*)-3,4,5,6-*tetrahydropyrimidine* (18).—2-(Phenacylthio)-3,4,5,6-tetrahydropyrimidine [8] (0.3 g) was heated under reflux for 2 h with chloroform (30 ml) and carbon disulphide (20 ml). Evaporation of the resulting solution and recrystallisation of the product from chloroform–light petroleum gave 5,6-dihydropyrimido-[2,1-*c*][1,2,4]dithiazole-3(7*H*)-thione (0.15 g), m.p. 154 °C, identical with the sample previously prepared (Found: C, 31.8; H, 3.1; N, 14.7%).

Treated with phenyl isothiocyanate (2.0 g) for 1 h at 100 °C, the (phenacylthio)tetrahydropyrimidine (1 g) gave 2,3,4,5-tetrahydro-1,6-diphenyl-3,4-propano-6aλ⁴-thia-1,3,4,6-tetra-azapentalene-2,5-dithione (1.2 g) as colourless prisms, m.p. 180 °C, from chloroform–light petroleum (Found: C, 56.2; H, 4.5; N, 14.7%). The same product was obtained in 86% yield from 2-(phenacylthio)-3,4,5,6-tetrahydropyrimidine hydrobromide, by treatment with phenyl isothiocyanate in the presence of aqueous methanolic sodium hydrogencarbonate.

Methyl isothiocyanate (2 g) reacted exothermically with 2-(phenacylthio)-3,4,5,6-tetrahydropyrimidine (1 g) at room temperature. The solid product, crystallised from chloroform–light petroleum gave 2,3,4,5-*tetrahydro*-1,6-*dimethyl*-3,4-*propano*-6aλ⁴-*thia*-1,3,4,6-*tetra-azapentalene*-2,4-*dithione* (19) as colourless needles (1 g), m.p. 203—205 °C; $\lambda_{max.}$(EtOH) 242 and 261 nm (ε 16 800 and 34 400); δ($CDCl_3$) 2.36 (2 H, m), 3.02 (6 H, s), and 4.40 (4 H, t); *m/e* 260 (M^+) (Found: C, 36.9; H, 4.6; N, 21.4; S, 36.9. $C_8H_{12}N_4S_3$ requires C, 36.9; H, 4.6; N, 21.5; S, 36.9%). The same product was obtained in 84% yield by heating 5,6-dihydropyrimido[2,1-*c*][1,2,4]dithiazole-3(7*H*)-thione with methyl isothiocyanate in chloroform for 2 h.

2-(Phenacylthio)-3,4,5,6-tetrahydropyrimidine (1 g) and phenyl isocyanate (1.3 g) were heated under reflux in benzene (50 ml) for 30 min. The reaction mixture was filtered to remove *NN'*-diphenylurea and the product was isolated by preparative t.l.c. on silica, with chloroform–ethyl acetate (1 : 1) as the mobile phase. The major band was removed and the product extracted with methanol. Crystallisation from chloroform–light petroleum gave 2,3,4,5-tetrahydro-1,6-diphenyl-3,4-propane-6aλ⁴-thia-1,3,4,6-tetra-azapentalene-2,5-dione as colourless needles (0.25 g), m.p. 209 °C, identical with the sample previously prepared.

Sublimation Experiments.—2,3,4,5-Tetrahydro-2,5-bis-(phenylimino)-3,4-ethano-1,6,6aλ⁴-trithia-3,4-diazapentalene and 2,3,4,5-tetrahydro-1,6-diphenyl-3,4-propano-6aλ⁴-thia-1,3,4,6-tetra-azapentalene-2,5-dithione both sublimed under reduced pressure (0.2 mmHg, bath temperature 160—180 °C) with little decomposition. Under similar conditions (bath temperature 150 °C) 2,3,4,5-tetrahydro-1,6-dimethyl-3,4-propano-6aλ⁴-thia-1,3,4,6-tetra-azapentalene-2,5-dithione (1 g) gave a colourless product (0.3 g), m.p. *ca.* 189 °C, thought to be impure 2,3,5,6-tetrahydro-2-methylpyrimido[2,1-*b*][1,2,4]thiadiazole-3(7*H*)-thione; δ($CDCl_3$) 2.36 (2 H, m), 3.26 (3 H, s), 4.43 (4 H, t) (Found: C, 38.0, 38.5; H, 5.3, 4.6; N, 21.7. $C_6H_9N_3S_2$ requires C, 38.5; H, 4.9; N, 22.4%). This product reacted with methyl isothiocyanate (1 h at 80—100 °C) to regenerate the original dithione, isolated after recrystallisation in 69% yield. The supposed pyrimido-thiadiazolethione also reacted immediately with carbon disulphide in chloroform to give an unstable yellow adduct.

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