Organic Heterocyclothiazenes. Part 11.[1] Dithiatetrazocines and Dithiadiazolium Chlorides

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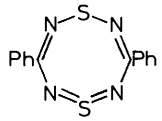
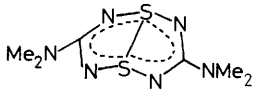
A reinvestigation of the reaction of benzamidine with sulphur dichloride failed to increase the yield of 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine (**1**) but uncovered a new product, 4-phenyl-1,2,3,5-dithiadiazolium chloride (**4**). This salt is the major product of reaction of tris(trimethylsilyl)benzamidine (**3**) with sulphur dichloride (60%) or of benzamidine with disulphur dichloride (54%), the latter providing a particularly convenient route to (**4**). Benzamidine also reacts with S_4N_4 to give dithiatetrazocine (**1**), but the best synthesis of (**1**) so far available involves treatment of benzamidine with a mixture of bis-(*p*-tolylsulphonyl)sulphurdi-imide (**5**) and diphthalimimido sulphide (**6**); other products of this reaction are the 1,2,4,6-thiatriazines (**7**) and (**8**). Benzamidoxime and sulphur dichloride also give dithiatetrazocine (**1**) and dithiadiazolium chloride (**4**). 2-Furylamidine and 2-thienylamidine give the analogous dithiatetrazocines (**9**) and (**10**), and dithiazolium chlorides (**11**) and (**12**). Treatment of a mixture of benzamidine and dimethylguanidine with sulphur dichloride gives the first unsymmetrical dithiatetrazocine (**13**). The u.v. spectra of the diaryldithiatetrazocines [(**1**), (**9**), (**10**)] are all very similar, and typically 'aromatic', indicating the same planar, delocalized heterocyclic ring structure, but are very different from those of the dimethylamino derivatives (**2**) and (**13**) which have folded structures. Thus one dimethylamino substituent is sufficient to buckle the planar dithiatetrazocine ring. Dithiatetrazocine (**1**) is unreactive (no reaction with MCPBA, N_2O_4, chloramine-T, Ph_3P, or CH_2N_2) but is reduced to benzamidine with hydrazine and palladium, and is oxidised by ozone, followed by ring contraction to give the thiatriazine (**8**). Mechanisms are suggested for new key reactions.

In an attempted synthesis of a linear polymeric conductor based on the structure of polysulphur nitride, Woodward and co-workers condensed benzamidine with sulphur dichloride.[2] This reaction proved to be complex giving none of the desired polymer but only a small amount (7.4%) of a yellow crystalline solid, 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine (**1**). This interesting 8-membered heterocyclic ring system was perfectly planar, with all S–N bonds of the same length, as were all the C–N bonds, indicating that the ring is a delocalised (10π) aromatic system. This was supported by the long wavelength u.v. absorptions, typical of an aromatic system, and by the striking chemical inertness of the compound towards *m*-chloroperbenzoic acid, sodium hexamethyldisilazane, and butyllithium. The corresponding *p*-methoxyphenyl and *p*-ethoxycarbonylphenyl derivatives were made in the same way, in even lower yields, and their structures were entirely analogous to that of the diphenyl compound (**1**),[2] as was the di-t-butyl compound, synthesised later in somewhat better yield (13.7%).[3] Attempts to prepare the parent dithiatetrazocine were unsuccessful, but the reaction of *N*,*N*-dimethylguanidine with sulphur dichloride gave the corresponding 3,7-bis(dimethylamino) compound in much better yield (54%). However, the u.v. spectrum of this product was very different from that of the aryl substituted compounds, and *X*-ray diffraction showed that the heterocyclic ring was no longer planar, but folded about an axis through the two sulphur atoms with an interplanar angle of 101°.[2] The transannular S–S distance in (**2**) was 2.43 Å, compared to 3.79 Å in (**1**). Thus the electron-rich planar aromatic ring structure, presumably destabilized by the strongly electron-releasing groups, had buckled to a folded structure with partial S–S bonding.

We set out to improve the synthesis of the dithiatetrazocine ring system, to explore its chemistry, and to synthesize some related derivatives. Whilst we have not been able to increase the dithiatetrazocine yields substantially we have simplified and extended the synthesis, and identified the major product of the benzamidine–sulphur dichloride reaction.



(**1**)

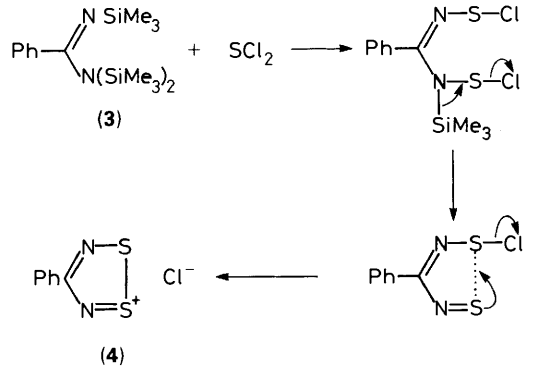


(**2**)

Synthesis of Dithiatetrazocine (**1**).—(a) *From benzamidine.* We first tried to improve the yield of compound (**1**) by altering the reported conditions.[2] Addition of sulphur dichloride over a longer period of time (1 h), lowering of the reaction temperature (−10 °C), or using a high dilution technique all made very little difference. However we did isolate a product not reported by the earlier workers,[2] the yellow, air-sensitive 4-phenyl-1,2,3,5-dithiadiazolium chloride (**4**) (10—15%), identical with an authentic specimen.[4] When benzamidine was replaced by its tris(trimethylsilyl) derivative (**3**) we obtained a much better yield of the dithiadiazolium salt (**4**) (60%) and very little (**1**) (6%). A mechanism for the formation of (**4**) from benzamidine or its silylated derivative (shown) is suggested in Scheme 1.

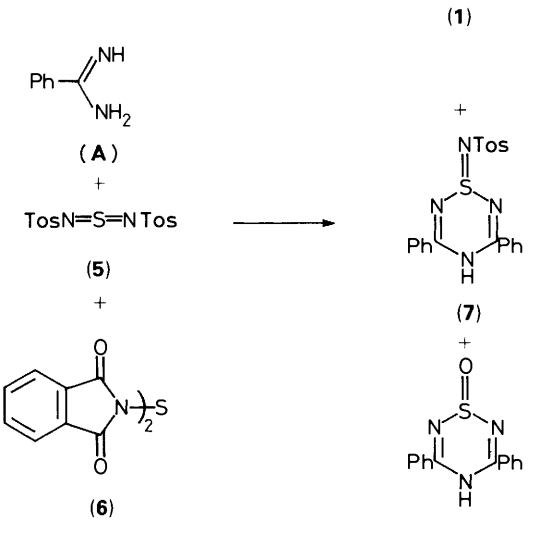
Dithiadiazolium chlorides have been prepared from trithiazyl trichloride and nitriles[4] or aldazines,[5] from benzonitrile, ammonium chloride and sulphur dichloride,[4] and from benzamidinium chloride and sulphur dichloride in hot nitrobenzene.[4] Our reactions of benzamidine, particularly with disulphur dichloride (below), compare favourably with these methods, in terms of mildness, convenience, and yields.

In further attempts to improve the preparation of dithiatetrazocine (**1**) we explored the reactions of benzamidine with other sulphur transfer reagents. When the amidine hydrochlor-



Scheme 1.

Table. Reaction of benzamidine (A) with reagents (5) and (6)



(A):(5):(6)	Method[a]	Time (h)	% Yield (1)	% Yield (7)	% Yield (8)
2:1:1	A	40	9.6	11	15
2:1:1	B	20	7.4	2	22
2:1:10	A	20	8.4	5	18
2:1:6	C	15	9.4	4	21
1:1:3	C	20	8.6	3	15

[a] See Experimental section.

ide was treated with disulphur dichloride in dichloromethane at room temperature in the presence of diazabicycloundecene (DBU), phenyldithiadiazolium chloride (**4**) was precipitated as the major product (54%) and only 2.6% of compound (**1**) was obtained.

Since tetrasulphur tetranitride, S_4N_4, can be used to introduce the sulphur di-imide unit when treated with organic amines and imines,[6] it seemed a promising reagent for the conversion of benzamidine into the cyclic bis(sulphur di-imide) (**1**). When benzamidine and S_4N_4 were heated under reflux in benzene, toluene, or xylene, compound (**1**) was indeed formed, though again in low yield (up to 7.4%), together with 2,4,6-triphenyl-1,3,5-triazine and benzonitrile. The reaction of benzamidine and S_4N_4 in dichloromethane at room or reflux temperature in the presence of titanium tetrachloride or lead tetra-acetate gave mainly baseline products, and only trace amounts of dithiatetrazocine (**1**).

Sulphur transfer reagents of the type R_2NSCl and R_2NSNR_2, with nitrogen heterocyclic rings as the leaving groups, have been developed as alternatives to sulphur dichloride[7] for the synthesis of sulphur-containing heterocyclic compounds.[8] However when benzamidine was treated with a range of these reagents (R_2NH = piperidine, morpholine, phthalimide, and succinimide), dithiatetrazocine (**1**) was formed in only minute amounts (< 1%). Similarly when benzamidine was treated with various sulphur di-imides, compound (**1**) was again formed but only in very low yield. The best reagent was bis(*p*-tolylsulphonyl)sulphur di-imide (**5**) which gave a 6% yield of (**1**) in dichloromethane at room temperature; product isolation consisted simply of removal of the toluene-*p*-sulphonamide by filtration, evaporation of solvent, and chromatography.

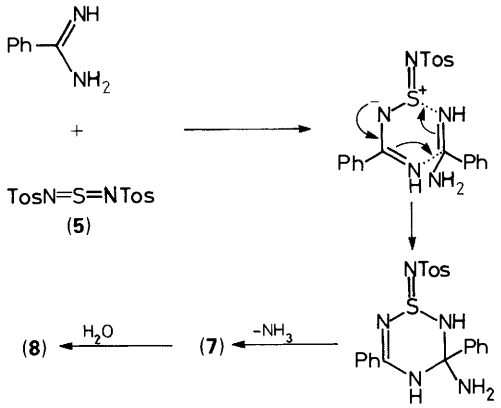
Formation of dithiatetrazocine (**1**) in the above reactions with divalent or tetravalent sulphur reagents requires an oxidation or reduction step, respectively, since (1) formally contains one divalent and one tetravalent sulphur atom. The correct oxidation level could be achieved by an equimolar mixture of a divalent (R_2NSNR_2) and a tetravalent (RN=S=NR) reagent, and this procedure did give slightly better yields of (**1**). The best combination was found to be bis(phthalimido sulphide) (**6**) and the tosyl di-imide (**5**), and their reaction with benzamidine was studied in some detail (Table 1). Slow addition of a solution of benzamidine in dry dichloromethane at room temperature under nitrogen, to a stirred mixture of sulphur di-imide (**5**) and phthalimido sulphide (**6**) gave (**1**) (7.4%). When the sulphur di-imide (**5**) was added to benzamidine and an excess of sulphide (6), previously stirred together, the yield was 8.4%. A slightly better yield (9.6%) was obtained when a solution of benzamidine was added to a stirred slurry of sulphide (**6**), followed by addition of sulphur di-imide (**5**), all in dry dichloromethane. Refluxing the mixture of benzamidine and an excess of sulphide (6) in dichloromethane for 3 h, cooling to room temperature, followed by slow addition of sulphur di-imide (**5**), gave 9.4% of compound (**1**); in refluxing chloroform 8.6% was obtained.

The best method currently available for the synthesis of dithiatetrazocine (**1**) is thus the addition of benzamidine to a stirred slurry of sulphide (**6**) in dichloromethane at room temperature, followed by slow addition of sulphur di-imide (**5**). Both reagents are easy to make and purify, and are cheap and stable. The work-up is simple since no sulphur is formed to complicate the chromatography, and no base is needed.

Two other compounds were isolated from these reactions of benzamidine with reagents (**5**) and (**6**): 3,5-diphenyl-1-(*p*-tolylsulphonylimino)-1,2,4,6-thiatriazine (**7**) and its hydrolysis product 1-hydroxy-3,5-diphenyl-1,2,4,6-thiatriazine (**8**). Compound (**7**) was converted into (**8**) during chromatography, and their combined yields were fairly constant at *ca.* 25% (Table). Structures (**7**) and (**8**) were based on elemental analysis and spectral data; in particular the i.r. spectrum of (**7**) showed four absorptions at 1 260, 1 130, 1 080, and 985 cm^{-1} characteristic of arenesulphonylsulphilimines. The sulphilimine (**7**) is thus the major (initial) product of this reaction, and is presumably formed from benzamidine and sulphur di-imide (**5**) by a mechanism, such as that shown in Scheme 2, where six-membered ring formation is understandably favoured over formation of the eight-membered ring of compound (**1**).

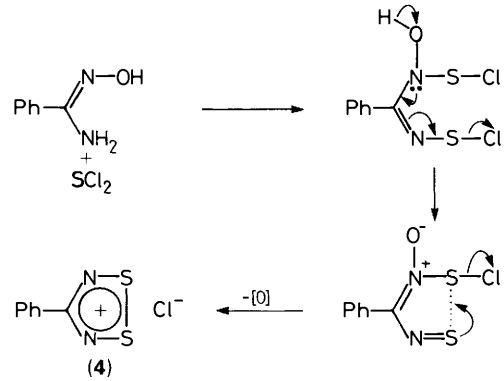
(b) *Reactions of benzamidoxime.* Like benzamidine, benzamidoxime has an N–C–N function suitable for the formation of the dithiatetrazocine (**1**), and since it is at a higher oxidation level it can lead directly to a heteroaromatic species. So it might react more readily with the divalent sulphur reagents, initially to form the mono-*N*-oxide of (**1**) though this could well be deoxygenated under the reaction conditions.

When benzamidoxime was treated with sulphur dichloride in



Scheme 2.

the presence of DBU, dithiatetrazocine (**1**) was formed in a yield (6%) similar to that of the benzamidine reaction, together with much more 4-phenyl-1,2,3,5-dithiazolium chloride (**4**) (32%). This could have been formed by a mechanism analogous to that for benzamidine or its tris(trimethylsilyl) derivative (Scheme 1) but with a final deoxygenation by sulphur dichloride (Scheme 3).

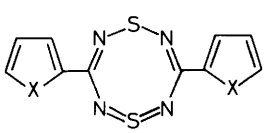


Scheme 3.

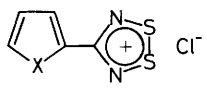
In contrast, the reaction of benzamidoxime with disulphur dichloride was very complex and the only isolable product was sulphur. Even the reaction of the amidoxime with bis(*p*-tolylsulphonyl)sulphur di-imide (**5**) failed and only benzonitrile and starting amidoxime were isolated.

Like benzamidine, benzamidoxime reacted with S_4N_4 to give dithiatetrazocine (**1**) but the reaction was slower and the yields slightly lower, thus offering no advantage. Other products were the thiatriazine *S*-oxide (**8**) and the corresponding *S*,*S*-dioxide, and 3,5-diphenyl-1,2,4-triazole.

Other 1,5,2,4,6,8-*Dithiatetrazocines*.—We attempted to apply the above methods, for the conversion of amidines into dithiatetrazocines, to the amidines, $RC(=NH)NH_2$, (R = CO_2H, CO_2Me, Me, CH_2OH) but all to no avail. Where R = CO_2H, the amidine was remarkably inert, but with all the others the reactions were too complex for the isolation of crystalline products. However we were able to prepare the 2-furyl and 2-thienyl analogues, (**9**)—(**12**), of dithiatetrazocine (1) and dithiadiazolium chloride (**4**) by these methods.



(**9**) X = O
(**10**) X = S



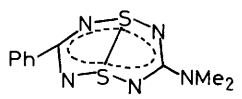
(**11**) X = O
(**12**) X = S

When 2-furylamidine was treated with sulphur dichloride in dichloromethane at 0 °C in the presence of DBU, the major product was a burgundy coloured air-sensitive crystalline compound. The mass spectrum showed it to be a mixture of 4-(2-furyl)-1,2,3,5-dithiazolium chloride (**11**) and its monochloro derivatives. A minor crystalline product was also isolated and its mass spectrum, and h.p.l.c. (MeOH), suggested that it was a mixture of polychlorinated derivatives of the dithiatetrazocine (**9**). The problem of polychlorination was overcome by treating the furylamidine with S_4N_4 in boiling xylene. A very low yield (2%) of 3,7-di-2-furyl-1,5,2,4,6,8-dithiatetrazocine (**9**) was obtained, together with 2,4,6-tri-2-furyl-1,3,5-triazine and furan-2-carbonitrile. Compound (**9**) was a deep yellow, high melting solid, only slightly soluble in most organic solvents. The mass spectrum showed the molecular ion, and major fragment ions corresponding to the loss of furan-2-carbonitrile and N, furan-2-carbonitrile and N_2S, and furan-2-carbonitrile and N_2S_2. The ^1H n.m.r. showed multiplets at δ 7.63, 7.24, and 6.89, all with equal integrals. The u.v. spectrum had $\lambda_{max.}$(EtOH) at 272, 323, 338, and 448 nm similar to that of the diphenyl compound (1), indicating a similar planar structure for the dithiatetrazocine ring in (**9**). Compound (**9**) was also formed, in very low yield, from 2-furylamidine and sulphur di-imide (**5**). No chlorination of compound (**9**) occurred when it was treated with an excess of sulphur dichloride at room temperature; hence chlorination of the furan rings, noted above, presumably occurred before dithiatetrazocine ring formation.

Similar treatment of 2-thienylamidine with sulphur dichloride gave 4-(2-thienyl)-1,2,3,5-dithiadiazolium chloride (**12**), a red crystalline air-sensitive solid, as the major product (69%). Its mass spectrum showed the molecular ion of the cation, with major fragments for the loss of NS and NS_2. 3,7-Di-2-thienyl-1,5,2,4,6,8-dithiatetrazocine (**10**) was also obtained, uncontaminated with chlorinated derivatives, though prolonged stirring of the reaction mixture at room temperature did lead to the formation of polychlorinated derivatives.

Dithienyldithiatetrazocine (**10**) is an orange-yellow, high-melting, crystalline solid, only slightly soluble in most organic solvents. Its mass spectrum showed the molecular ion, with major fragments for the loss of thiophene-2-carbonitrile, thiophene-2-carbonitrile and N, thiophene-2-carbonitrile and N_2S, and thiophene-2-carbonitrile and N_2S_2. The ^1H n.m.r. spectrum showed double doublets at δ 8.30, 7.64, and 7.23, all with equal integrals; the u.v. spectrum had $\lambda_{max.}$(EtOH) at 271, 318, 351, and 447 nm, very similar to the spectra of dithiatetrazocines (1) and (**9**), again indicating the planarity of the heteroaromatic ring. Treatment of 2-thienylamidine with sulphur di-imide (**5**) gave dithiatetrazocine (**10**) in very low yield (1.7%), and treatment with S_4N_4 in boiling xylene also gave (**10**) (3.5%) together with thiophene-2-carbonitrile and 2,4,6-tri-2-thienyl-1,3,5-triazine (11%).

Finally we synthesized the first unsymmetrically substituted dithiatetrazocine (**13**) to see if one dimethylamino group is sufficiently electron releasing to convert the planar dithiatetrazocine into the folded structure [*cf.* (**2**)]. When a mixture of benzamidine and *N*,*N*-dimethylguanidine was treated as before with sulphur dichloride, 3,7-diphenyl-, 3,7-bis(dimethylamino)-, and 3-(dimethylamino)-7-phenyl-1,5,2,4,6,8-dithiatetrazocines, (**1**) (9.5%), (**2**) (5%), and (**13**) (3%), respectively, were obtained.



(**13**)

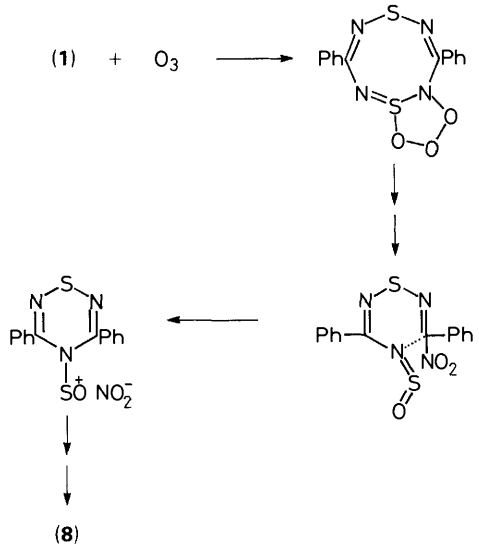
Curiously, the combined yield (17.5%) of dithiatetrazocines in this mixed experiment was the highest that we observed.

The unsymmetrical compound (**13**) was obtained as pale yellow crystals, readily soluble in organic solvents. The mass spectrum showed a molecular ion and major fragment ions for the loss of Me_2NCN_2, Me_2NCN_2 and NS, and Me_2NCN_2 and NS_2, and the ^1H n.m.r. showed the expected aromatic multiplets and a singlet for the methyl protons at δ 3.21 [*cf.* 3.15 for (**2**)].[2] The u.v. spectrum showed $\lambda_{max.}$ at 250 nm, similar to that of the bis(dimethylamino) compound (**2**), and completely lacking the complex long wavelength absorptions of the diaryl compounds (**1**), (**9**), and (**10**). This strongly suggests that the mono-amino derivative (**13**) has a folded structure similar to that of the diamine (**2**) and that one dimethylamino group is sufficient to buckle the planar heterocyclic ring.

Chemistry of the Dithiatetrazocines.—Woodward and co-workers[2] had shown that the diphenyl compound (**1**) was thermally stable, resistant to nucleophiles, and not oxidized by MCPBA in boiling dichloromethane. It is also stable to MCPBA in boiling 1,2-dichloromethane and to dinitrogen tetraoxide in dichloromethane. No adduct was formed with norbornadiene in boiling water, and (**1**) was inert towards diazomethane. Nor did it react with triphenylphosphine in boiling xylene or chloramine-T in boiling methanol. All this accords well with its 10π aromatic stability. Although it was stable to anhydrous hydrazine at room temperature, the addition of a catalytic amount of 10% palladium on charcoal caused the reduction of (**1**) to benzamidine (75%) and sulphur. When ozone was passed through a slurry of (**1**) in dichloromethane at −78 °C for 30 min, followed by chromatography on silica, 1-hydroxy-3,5-diphenyl-1,2,4,6-thiatriazine (**8**) (32%) and the corresponding *S*,*S*-dioxide (3%) were formed; ozonolysis for 60 min gave slightly increased yields (38 and 5% respectively). A possible mechanism for this ring contraction reaction is shown in Scheme 4. Ozonolysis of a sulphimide bond could, after rearrangemment, lead to a nitrosulphinylamine intermediate, analogous to the ozonolysis of an iminophosphorane to a nitro compound and a phosphine oxide.[9] Intramolecular displacement of nitrite, further oxidation at sulphur and a final hydrolysis could lead to the isolated products.

Since the dithiatetrazocine ring was so stable to MCPBA and N_2O_4, we planned to oxidize the thiophene rings in the dithienyl compound (**10**) to the sulphoxide or sulphone, and to degrade these rings further, as an approach to the parent ring system. However, attempted oxidation of compound (**10**) with MCPBA in boiling 1,2-dichloroethane, or with N_2O_4, failed to give any *S*-oxides; in all cases (**10**) was recovered (80—90%). Similarly, on attempted nitration of (**10**) with nitronium tetrafluoroborate in ether or acetonitrile, starting material was recovered (90—95%). This inertness was surprising since we had assumed that the 'π-excessive' dithiatetrazocine ring would not be a strongly electron-withdrawing substituent on the thiophene ring.

Finally, since the two sulphur atoms in the folded structure (**2**) are relatively close to each other (2.43 Å), even closer than in S_4N_4 (2.60 Å), and since they readily add chlorine, from chlorine gas[10] or sulphuryl chloride,[11] we thought that (**2**) might undergo cycloaddition reactions. However it failed to react with diazomethane, dimethyl acetylenedicarboxylate, norbornadiene, or phenyl vinyl sulphoxide, under fairly vigorous conditions, thus indicating that in spite of the folded structure of the ring, (**2**) still retains some aromatic stability.



Scheme 4.

Experimental

All solvents were dried thoroughly and stored under dry nitrogen. Light petroleum refers to the fraction, b.p. 40—60 °C, unless stated otherwise. All petroleum fractions were redistilled through a 36 cm Vigreux column prior to use. Ether and tetrahydrofuran (THF) were dried by distillation from potassium–benzophenone ketyl. Benzene, toluene, and xylene were pre-dried over sodium wire and then distilled from calcium hydride. Dichloromethane, 1,2-dichloroethane, chloroform, and tetrachloromethane were dried by distillation from phosphorus pentaoxide and stored over 3 A molecular sieves. Chloroform was passed over Brockmann Grade 1 basic alumina immediately prior to use. Acetontrile was dried by distillation from calcium hydride under nitrogen. Sulphur dichloride was distilled from phosphorus pentachloride at atmospheric pressure under nitrogen directly before use. Disulphur dichloride was distilled from sulphur and charcoal, the fraction, b.p. 135—137 °C, being stored in a dark container in the refrigerator. Chromatography refers to medium pressure (hand bellows) column chromatography on silica (Merck Kieselgel 60 H) of the pre-adsorbed mixture. Columns were eluted with light petroleum and then 5%, 10%, 15%, *etc.* of dichloromethane in light petroleum. For other general points see ref. 12.

Reactions of Benzamidine.—Benzamidine was liberated from its hydrochloride salt with aqueous sodium hydroxide (5M) and extracted into dichloromethane; the solution was dried with magnesium sulphate, filtered, and the solvent evaporated to give benzamidine, m.p. 67—69 °C.

(*i*) *With sulphur dichloride.* A solution of sulphur dichloride (1.35 ml, 2.19 g, 21.25 mmol) in dichloromethane (20 ml) was added dropwise over 1 h to a stirred solution of benzamidine (1.70 g, 14.17 mmol) and DBU (6.35 ml, 42.5 mmol) in dry dichloromethane at 0 °C under nitrogen. When the addition was complete the reaction mixture was stirred for a further 2 h at 0 °C and then at room temperature for 1 h. A flocculent air-sensitive yellow precipitate [identified as 4-phenyl-1,2,3,5-dithiadiazolium chloride (**4**) (10%) as described below] was removed by filtration under nitrogen, and then the solvent was evaporated and the residue chromatographed on silica. Elution with light petroleum gave sulphur and with 10% dichloromethane in light petroleum, 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine (**1**) (127 mg, 6%) was obtained as yellow plates, m.p. 224—225 °C (lit.,[2] 225—226 °C); $\lambda_{max.}$(EtOH) 274 (ε 26 400), 283 (26 100), 297.5 (29 700), 310 (37 500), 323 (28 900), and 414 nm (7 200); $\nu_{max.}$(Nujol mull) 1 595, 1 485, 1 450, 1 365, 1 320, 1 298, 1 233, 1 160, 1 030, 1 000, 970, 940, 925, 780, and 690 cm^{-1};

δ_H(400 MHz, CD_2Cl_2) 7.46—7.51 (m), 7.545—7.60 (m), and 8.53—8.57 (dd); *m/z* (190 °C) 298 (M^+, 24%), 195 (M^+ − PhCN, 6), 181 (M^+ − $PhCN_2$, 5), 167 (2), 149 ($PhCN_2S^+$, 9), 135 ($PhCNS^+$, 100), 103 (PhCN, 41), 77 (Ph^+, 14), 64 (S_2, 22), and 46 (NS, 62).

The above reaction was repeated at −10 °C; 4-phenyl-1,2,3,5-dithiadiazolium chloride (**4**) (15%) and dithiatetrazocine (**4a**) (5.5%) were obtained by a similar work-up procedure.

A solution of benzamidine (0.72 g, 6 mmol) in dichloromethane (50 ml) and a solution of sulphur dichloride (0.93 g, 0.60 ml, 9 mmol) in dichloromethane (50 ml). were added synchronously and dropwise over 10 h to a large flask containing dichloromethane (1.5 l) and DBU (2.74 g, 2.7 ml, 18 mmol) which was vigorously stirred under nitrogen at room temperature. When the addition was complete the mixture, a cloudy orange–brown solution, was stirred for a further 15 h after which the solvent was evaporated and the residue chromatographed on silica as described above to give sulphur and dithiatetrazocine (**1**) (61 mg, 6.8%).

(*ii*) *With disulphur dichloride.* To a stirred suspension of benzamidinium chloride (2.4 g, 15.33 mmol) and DBU (7 g, 6.9 ml, 46 mmol) in dichloromethane (45 ml), a solution of disulphur dichloride (1.84 ml, 23 mmol) in dichloromethane (20 ml) was added dropwise over 30 min at 0 °C under nitrogen. The resulting dark red-brown reaction mixture was stirred for a further 2 h at 0 °C and then for 3 h at room temperature. The yellow precipitate of dithiadiazolium chloride (**4**) (1.78 g, 54%) was removed by filtration under nitrogen, and then the solvent was evaporated and the residue chromatographed on silica as described above to give dithiatetrazocine (**1**) (59 mg, 2.6%).

(*iii*) *With tetrasulphur tetranitride: typical procedure.* S_4N_4 (423 mg, 2.3 mmol) and benzamidine (821 mg, 6.84 mmol) were heated at reflux in toluene (50 ml) under nitrogen for 15 h. Methanol (5 ml) was added to homogenise the mixture and then the solvent was evaporated and the residue chromatographed on silica. Elution with light petroleum gave sulphur and with 20% chloroform in light petroleum, 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine (**1**) (63 mg, 6%) followed by 2,4,6-triphenyl-1,3,5-triazine (28 mg, 4%), m.p. 225—230 °C (identical with an authentic specimen) and benzonitrile were obtained.

The above reaction was repeated at reflux in benzene (16 h), toluene (3.5 h), and xylene (6 h) to give respectively compound (**1**) (3%, 7.4%, 6.5%) and the triazine (3%, 0%, 9%).

(*iv*) *With bis*-p-*tolylsulphonylsulphur di-imide* (**5**). To a stirred solution of benzamidine (0.76 g, 6.3 mmol) in dichloromethane (40 ml) was added dropwise over 30 min a solution of the title compound (**5**) (2.3 g, 6.3 mmol) in dichloromethane (40 ml), while the reaction mixture was stirred under nitrogen at room temperature. The red–brown cloudy reaction mixture was further stirred at room temperature for 102 h, after which it was filtered and evaporated and the residue chromatographed on silica. Elution with 10% dichloromethane in light petroleum gave dithiatetrazocine (**1**) (57 mg, 6.1%).

(*v*) *With bis*-p-*tolylsulphonylsulphur di-imides* (**5**) *and diphthalimido sulphide* (**6**). Method A. To a stirred suspension of diphthalimido sulphide (**6**) (1.8 g, 5.5 mmol) in dichloromethane (40 ml) was added at room temperature under nitrogen, a solution of benzamidine (1.32 g, 11 mmol) in dichloromethane (20 ml), dropwise over 10 min. After 30 min a solution of ditosylsulphur di-imide (**5**) (2.6 g, 7 mmol) in dichloromethane (40 ml) was added dropwise over 20 min to the reaction mixture at room temperature under nitrogen. The resulting mixture was further stirred at room temperature for 40 h after which it was filtered and evaporated and the residue chromatographed on silica. Elution with 10% dichloromethane in light petroleum gave dithiatetrazocine (**1**) (158 mg, 9.6%). Elution with ether gave 1-*hydroxy*-3,5-*diphenyl*-1,2,4,6-*thiatriazine* (**8**) (223 mg, 15%), m.p. 156—158 °C (Found: C, 62.2; H, 4.1: N, 15.6%; M^+, 269.0618. $C_{14}H_{11}N_3OS$ requires C, 62.4; H, 4.1; N, 15.6%; *M*, 269.0623); $\nu_{max.}$(Nujol mull) 3 380, 1 622, 1 618, 1 600, 1 590, 1 565, 1 455, 1 275, 1 070, 1 030, 990, 930, 735, 720, 712, 690, 670, and 620 cm^{-1}; δ_H(90 MHz, [$^2H_6$]DMSO) 7.50—7.70 (6 H, m), 8.20—8.35 (4 H, m), and 10.03 (1 H, s, br); *m/z* (160 °C) 269 (M^+, 5%), 253 (M^+ − O, 37), 252 (M^+ − OH, 25), 221 (M^+ − SO, 19), 149 ($PhCN_2S^+$, 15), 135 ($PhCNS^+$, 4), 118 ($PhCHN_2^+$, 12), 104 ($PhCHN^+$, 100), 103 (PhCN, 52), 91 (3), 77 (Ph^+, 26), and 46 (NS, 37). Elution with ethyl acetate gave 1-(p-*tolylsulphonylimino*)-3,5-*diphenyl*-1,2,4,6-*thiatriazine* (7) (247 mg, 11%), m.p. 156—158 °C (Found: C, 59.0; H, 4.2; N, 12.9. $C_{21}H_{18}N_4O_2S_2$ requires C, 59.7; H, 4.3; N, 13.3%); $\nu_{max.}$(Nujol mull) 1 610, 1 600, 1 590, 1 565, 1 280, 1 260, 1 130, 1 080, 1 015, 985, and 715 cm^{-1}; δ_H(250 MHz; [$^2H_6$]acetone) 2.35 (3 H, s), 7.20 (2 H, d, *J* 7.5 Hz), 7.48 (6 H, m), 7.80 (2 H, d, *J* 7.5 Hz), and 8.25 (4 H, m); *m/z* (200 °C) 253 (M^+ − TosN, 17%), 171 ($TosNH_2$, 44), 155 (Tos^+, 40), 149 ($PhCN_2S^+$, 7), 135 ($PhCNS^+$, 4), 104 ($PhCNH^+$, 43), 91 (100), 77 (Ph^+, 17), and 46 (NS, 10). For further results see Table.

Method B. To a stirred slurry of a mixture of ditosylsulphur di-imide (**5**) (720 mg, 1.95 mmol) and diphthalimido sulphide (**6**) (630 mg, 1.95 mmol) in 1,2-dichloroethane (20 ml), at room temperature under nitrogen, was added dropwise over 1 h a solution of benzamidine (468 mg, 3.9 mmol) in 1,2-dichloroethane (50 ml). The resulting mixture was stirred at room temperature for a further 20 h and then filtered, and evaporated. The residue was chromatographed on silica as described above to give dithiatetrazocine (**1**) (43 mg, 7.4%), hydroxythiatriazine (**8**) (115 mg, 22%), and 1-(*p*-tolylsulphonylimino)diphenylthiatriazine (**7**) (18 mg, 2%).

Method C. To a stirred slurry of the diphthalimido sulphide (**6**) (1.94 g, 6 mmol) in dichloromethane (50 ml) was added benzamidine (0.24 g, 2 mmol) and then the mixture was refluxed for 3 h under nitrogen. It was then cooled to room temperature, when a solution of ditosylsulphur di-imide (**5**) (0.37 g 1 mmol) in dry dichloromethane (30 ml) was added dropwise over 1 h. The resulting mixture was then further stirred at room temperature for 15 h after which it was filtered and the filtrate evaporated. The residue was chromatographed on silica as described above to give dithiatetrazocine (**1**) (28 mg, 9.4%), hydroxythiatriazine (**8**) (56 mg, 21%), and 1-(*p*-tolylsulphonylimino)diphenylthiatriazine (**7**) (17 mg, 4%).

Reaction of N,N,N′-*Tris*(*trimethylsilyl*)*benzamidine* (**3**) *with Sulphur Dichloride.*—To a stirred solution of *N,N,N′*-tris(trimethylsilyl)benzamidine (**3**)[13] (4.84 g, 14.36 mmol) in dichloromethane (100 ml) at 0 °C under nitrogen, was added dropwise over 2 h a solution of sulphur dichloride (1.4 ml, 21.54 mmol) in dichloromethane (100 ml). After 1 h, the cooling bath was removed and the reaction mixture was stirred at room temperature for 2 h. The yellow flocculent precipitate was collected by filtration under nitrogen to give 4-phenyl-1,2,3,5-dithiadiazolium chloride (**4**)[4] (1.87 g, 60%) as a fine yellow air-sensitive powder, $\lambda_{max.}$(CH_2Cl_2) 395 nm (ε 680); $\nu_{max.}$(Nujol mull) 1 600, 1 390, 1 340, 1 150, 1 070, 1 025, 1 000, 920, 890, 840, 780, 706, and 695 cm^{-1}; *m/z* (100 °C) 181 (M^+, 100%), 135 (M^+ − NS, 39), 117 ($PhCN_2^+$, 5), 103 (PhCN, 25), 89 (25), 78 (NS_2, 94), 77 (Ph^+, 21), and 46 (NS, 9). The solvent was removed under reduced pressure and the residue chromatographed on silica. Elution with light petroleum gave sulphur and with 20% dichloromethane in light petroleum, dithiatetrazocine (**1**) (128 mg, 6%) was obtained.

Reactions of Benzamidoxime.—(*i*) *With sulphur dichloride.* To a solution of benzamidoxime (2.14 g, 15.7 mmol) and DBU (7 ml, 47 mmol) in dichloromethane (45 ml), a solution of sulphur dichloride (1.5 ml, 23.5 mmol) in dichloromethane (20 ml) was added dropwise over 10 min while the reaction mixture was

stirred under nitrogen in an ice–water bath. After 2 h, the cooling bath was removed and the resulting dark reaction mixture was stirred at room temperature for 2 h. The yellow precipitate of 4-phenyl-1,2,3,5-dithiadiazolium chloride (**4**) (1.09 g, 32%) was removed by filtration under nitrogen, the filtrate evaporated, and the residue chromatographed on silica. Elution with 10% dichloromethane in light petroleum gave dithiatetrazocine (**1**) (129 mg, 5.6%).

(*ii*) *With tetrasulphur tetranitride.* S_4N_4 (319 mg, 1.7 mmol) and benzamidoxime (472 mg, 3.4 mmol) were heated at reflux in toluene (20 ml) under nitrogen for 12 h. The solvent was evaporated and the residue chromatographed on silica. Elution with 50% dichloromethane in light petroleum gave dithiatetrazocine (**1**) (20 mg, 4%). Elution with 50% ether in light petroleum gave 3,5-diphenyl-1,2,4-triazole (6 mg, 2%) as colourless crystals, m.p. 194—195 °C (lit.,[14] 190 °C) (Found: C, 75.6; H, 5.0; N, 18.8. Calc. for $C_{14}H_{11}N_3$: C, 76.0; H, 5.0; N, 19.0%); $\nu_{max.}$(Nujol mull) 1 610, 1 560, 1 440, 1 180, 1 140, 1 000, 790, 730, 710, 700, and 690 cm^{-1}; δ_H(90 MHz, [$^2H_6$]acetone) 7.4—7.55 (3 H, m) and 8.1—8.2 (2 H, m); *m/z* (160 °C) 221 (M^+, 100%), 118 (M^+ − PhCN, 61), 105 (11), 91 (17), and 77 (Ph^+, 19) and in ether, hydroxythiatriazine (**8**) (48 mg, 10%) (identical spectral data with the earlier specimen) was obtained. Elution with ethyl acetate gave 3,5-diphenyl-1,2,4,6-thiatriazine 1,1-dioxide (80 mg, 16%).

3,7-*Di*-2-*furyl*-1,5,2,4,6,8-*dithiatetrazocine* (**9**).—2-Furylamidine was liberated from its hydrochloride[15] salt with aqueous sodium hydroxide (5M) and extracted into dichloromethane; the solution was dried with magnesium sulphate, filtered, and evaporated to give 2-furylamidine, m.p. 55—57 °C.

(*i*) *From 2-furylamidine and tetrasulphur tetranitride.* S_4N_4 (368 mg, 2 mmol) and 2-furylamidine (440 mg, 4 mmol) were heated at reflux in xylene (20 ml) under nitrogen for 4 h. The solvent was evaporated and the residue chromatographed on silica. Elution with light petroleum gave sulphur and with 5% dichloromethane in light petroleum, 3,7-*di*-2-*furyl*-1,5,2,4,6,8-*dithiatetrazocine* (**9**) (11 mg, 2%) was obtained as yellow plates (ethyl acetate), m.p. 214—216 °C (Found: C, 43.1; H, 2.25; N, 19.8%; M^+, 277.9923. $C_{10}H_6N_4O_2S_2$ requires C, 43.15; H, 2.2; N, 20.1%; *M* 277.9932); $\lambda_{max.}$(EtOH) 272 (ε 16 100), 323 (36 000), 338 (34 100), and 448 nm (5 000); $\nu_{max.}$(CCl_4) 3 735, 2 926, 2 855, 1 735, 1 577, 1 508, 1 490, 1 459, 1 428, 1 398, 1 368, 1 265, 1 158, and 1 017 cm^{-1}; δ_H(250 MHz, $CDCl_3$) 6.89 (1 H, m), 7.24 (1 H, m), and 7.63 (1 H, m); *m/z* (180 °C) 278 (M^+, 26%), 200 (M^+ − NS_2, 9), 172 (M^+ − $C_5H_3N_2O$, 44), 139 ($C_5H_3N_2OS^+$, 9), 125 ($C_5H_3NOS^+$, 13), 94 ($C_5H_4NO^+$, 22), 78 (NS_2, 6), and 46 (NS, 100). Elution with 50% dichloromethane in light petroleum gave furan-2-carbonitrile, followed by 2,4,6-tri-2-furyl-1,3,5-triazine (76 mg, 20%) as plates, m.p. 244—245 °C (lit.,[16] 238—240 °C) (Found: M^+, 279.0641. $C_{15}H_9N_3O_3$ requires 279.0644); $\nu_{max.}$(CCl_4) 2 926, 2 855, 1 585, 1 520, 1 480, 1 420, 1 356, 1 265, 1 197, and 1 012 cm^{-1}; δ_H(250 MHz, $CDCl_3$) 6.61 (1 H, dd, *J* 1.5 and 4 Hz), 7.62 (1 H, dd, *J* 1 and 4 Hz), and 7.715 (1 H, dd, *J* 1 and 1.5 Hz); *m/z* (180 °C) 279 (M^+, 62%) and 93 ($C_5H_3NO^+$, 100).

(*ii*) *From 2-furylamidine and ditosylsulphur di-imide* (**5**). To a stirred slurry of 2-furylamidinium chloride (1.46 g, 10 mmol) and DBU (1.52 g, 1.5 ml, 10 mmol) in dichloromethane (20 ml) at room temperature under nitrogen, was added dropwise over 30 min a solution of ditosylsulphur di-imide (**5**) (3.7 g, 10 mmol) in dichloromethane (20 ml). The dark reaction mixture was stirred for a further 3 h at room temperature after which it was filtered and evaporated, and the residue chromatographed on silica. Elution with 10% dichloromethane in light petroleum gave 3,7-di-2-furyl-1,5,2,4,6,8-dithiatetrazocine (**9**) (20 mg, 1.4%).

Treatment of 2-Furylamidinium Chloride with Sulphur Dichloride.—To a stirred slurry of 2-furylamidinium chloride (2.55 g, 17.5 mmol) and DBU (8 g, 7.8 ml, 52.5 mmol) in dichloromethane (50 ml) at 0 °C under nitrogen, was added dropwise over 30 min a solution of freshly distilled sulphur dichloride (2.7 g, 1.7 ml, 26.25 mmol) in dichloromethane (20 ml). After 3 h the cooling bath was removed and the reaction mixture was stirred at room temperature for 4 h. A burgundy coloured precipitate (330 mg), a mixture of 4-2-furyl-1,2,3,5-dithiadiazolium chloride (**11**) [*m/z* (80—180 °C) 171 (M^+, 78%), 125 (35), and 93 (20)] and 4-(chloro-2-furyl)-1,2,3,5-dithiadiazolium chloride [*m/z* (80—180 °C) 205 (M^+, 39%), 159 (16) and 127 (8)], was filtered off under nitrogen, and the filtrate evaporated. The residue was chromatographed on silica. Elution with 5% dichloromethane in light petroleum gave a yellow crystalline mixture of di-, tri-, and tetra-chlorinated derivatives of 3,7-di-2-furyl-1,5,2,4,6,8-dithiatetrazocine (**9**) (11 mg); $\nu_{max.}$(CCl_4) 2 928, 2 289, 1 550, 1 496, 1 382, 1 347, 1 250, 1 206, 1 154, 1 106, 1 066, 1 016, and 904 cm^{-1}; δ_H(250 MHz, $CDCl_3$) 6.4 (m) and 7.26 (m); *m/z* (190 °C) 416 (M^+ tetrachloro, 1%), 382 (M^+ trichloro, 21), 346 (M^+ dichloro, 35), 205 (6), 159 (100), 127 (33), and 46 (97).

3,7-*Di*-2-*thienyl*-1,5,2,4,6,8-*dithiatetrazocine* (**10**).—(*i*) *From 2-thienylamidine and sulphur dichloride.* To a stirred slurry of 2-thienylamidinium chloride[17] (1.63 g, 10 mmol) and DBU (4.6 g, 4.5 ml, 30 mmol) in dichloromethane (40 ml) at 0 °C under nitrogen, was added dropwise over 30 min a solution of sulphur dichloride (1.5 g, 0.95 ml, 15 mmol) in dichloromethane (20 ml). After 2 h, the cooling bath was removed and the reaction mixture was stirred at room temperature for 5 h. A flocculent red precipitate (see below) was removed by filtration under nitrogen, and the filtrate evaporated. The residue was chromatographed on silica. Elution with 50% dichloromethane in light petroleum gave 3,7-*di*-2-*thienyl*-1,5,2,4,6,8-*dithiatetrazocine* (**10**) (113 mg, 7.3%) as orange–yellow plates (ethyl acetate), m.p. 271—273 °C (Found: M^+, 309.9475. $C_{10}H_6N_4S_4$ requires 309.9475); $\lambda_{max.}$(EtOH) 271 (ε 7 200), 318 (12 900), 351 (6 600), and 447 nm (1 100); $\nu_{max.}$(CCl_4) 2 927, 2 854, 1 532. 1 509, 1 427, 1 377, and 1 036 cm^{-1}; δ_H(250 MHz, $CDCl_3$) 7.23 (1 H, dd, *J* 4 and 5 Hz), 7.64 (1 H, dd, *J* 1 and 5 Hz), and 8.3 (1 H. dd, *J* 1 and 4 Hz); *m/z* (200 °C) 310 (M^+, 57%), 201 (M^+ − C_5H_3NS, 6), 187 ($C_5H_3N_2S_3^+$, 3), 141 ($C_5H_3NS_2^+$, 100), 109 ($C_5H_3NS^+$, 36), 78 (NS_2, 7), and 46 (NS, 86).

The red precipitate was collected by filtration under nitrogen and washed with dichloromethane to give pure 4-(2-*thienyl*)-1,2,3,5-*dithiadiazolium chloride* (**12**) (1.53 g, 69%) as a fine red powder, m.p. 162—164 °C (Found: M^+, 186.9461. $C_5H_3{}^{35}ClN_2S_3$ requires 186.9458); *m/z* (150 °C) 187 (M^+, 100%), 141 (M^+ − NS, 55), 109 (C_5H_3NS, 41), 78 (NS_2, 98). and 46 (NS, 12).

When the above reaction was repeated with stirring of the reaction mixture at room temperature for 15 h, 4-(2-thienyl)-1,2,3,5-dithiadiazolium chloride (**12**) (30%), a mixture of mono-, di-, and tri-chlorinated 3,7-di-2-thienyl-1,5,2,4,6,8-dithiatetrazocines [*m/z* (200 °C) 414 (M^+ trichloro, 3%), 378 (M^+ dichloro, 29), 344 (M^+ monochloro, 100), 175 (60), 141 (89), 109 (50), and 46 (91)] and 3,7-di-2-thienyl-1,5,2,4,6,8-dithiatetrazocine (**10**) (2.9%) were obtained.

(*ii*) *From 2-thienylamidine and tetrasulphur tetranitride.* S_4N_4 (368 mg, 2 mmol) and 2-thienylamidine (504 mg, 4 mmol) (m.p. 61—63 °C, generated from the hydrochloride as described for furylamidine) were heated at reflux in xylene (40 ml) under nitrogen for 5 h. The solvent was evaporated and the residue chromatographed on silica. Elution with light petroleum gave sulphur and with 50% dichloromethane in light petroleum 3,7-di-2-thienyl-1,5,2,4,6,8-dithiatetrazocine (**10**) (22 mg, 3.5%) was obtained, followed by 2,4,6-tri-2-thienyl-1,3,5-triazine (48 mg, 11%) as a colourless compound, m.p. 196—198 °C (lit.,[16] 192—194 °C) (Found: M^+, 326.9941. $C_{15}H_9N_3S_3$ requires 326.9959);

$\nu_{max.}(CCl_4)$ 2 927, 1 532, 1 509, 1 427, 1 378, 1 334, 1 222, and 1 036 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.2 (1 H, dd, *J* 5.25 and 3.5 Hz), 7.6 (1 H, dd, *J* 5.25 and 1 Hz), and 8.26 (1 H, dd, *J* 3.5 and 1 Hz); *m/z* (160 °C) 327 (M^+, 97%) and 109 (C_5H_3NS, 100).

(*iii*) *From 2-thienylamidine and ditosylsulphur di-imide* (**5**). To a stirred slurry of 2-thienylamidinium chloride (1.8 g, 11 mmol) and DBU (1.7 g, 1.6 ml, 11 mmol) in dichloromethane (30 ml) at room temperature under nitrogen, was added dropwise over 30 min a solution of ditosylsulphur di-imide (**5**) (5.55 g, 15 mmol) in dichloromethane (20 ml). The orange–red reaction mixture was stirred at room temperature for 5 h after which it was filtered and the filtrate evaporated. The residue was chromatographed on silica. Elution with 50% dichloromethane in light petroleum gave 3,7-di-2-thienyl-1,5,2,4,6,8-dithiatetrazocine (**10**) (20 mg, 1.7%).

3-*Dimethylamino*-7-*phenyl*-1,5,2,4,6,8-*dithiatetrazocine* (**13**).—To a stirred mixture of benzamidine (1.2 g, 10 mmol), *N*,*N*-dimethylguanidine sulphate (1.36 g, 5 mmol), and DBU (7.6 g, 7.5 ml, 50 mmol) in dichloromethane (30 ml) at 0 °C under nitrogen, was added a solution of sulphur dichloride (3.1 g, 1.9 ml, 30 mmol) in dichloromethane (20 ml) dropwise over 10 min. After 1 h the cooling bath was removed and the dark reaction mixture was stirred at room temperature for 3 h. It was then filtered and evaporated, and the residue chromatographed on silica. Elution with light petroleum gave sulphur and with 10% dichloromethane in light petroleum, 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine (1) (141 mg, 9.5%) was obtained. Elution with dichloromethane gave 3-*dimethylamino*-7-*phenyl*-1,5,2,4,6,8-*dithiatetrazocine* (**13**) (80 mg, 3%) as a pale yellow crystalline compound, m.p. 182—183 °C (Found: C, 45.4; H, 4.4; N, 26.3%; M^+, 265.0452. $C_{10}H_{11}N_5S_2$ requires C, 45.3; H, 4.2; N, 26.4%; *M*, 265.0456); $\lambda_{max.}$(EtOH) 250 nm (ε 9 400); $\nu_{max.}(CCl_4)$ 2 927, 1 561, 1 456, 1 411, 1 372, 1 357, 1 243, 1 175, 1 146, 1 086, and 1 027 cm^{-1}; δ_H(250 MHz, $CDCl_3$) 3.21 (6 H, s), 7.35—7.5 (3 H, m), and 8.17 (2 H, dd, *J* 1.5 and 8.5 Hz); *m/z* (160 °C) 265 (M^+, 100%), 181 ($M^+ - C_3H_6N_3$, 20), 162 (M^+ − PhCN, 28), 135 ($PhCNS^+$, 11), 116 (M^+ − PhCN − NS, 25), 103 (PhCN, 14), 102 (22), 78 (NS_2, 21), 69 (23), and 46 (NS, 80). Elution with 5% ether in dichloromethane gave 3,7-bis(*N*,*N*-dimethylamino)-1,5,2,4,6,8-dithiatetrazocine (**2**) (59 mg, 5%).

Reactions of 3,7-*Diphenyl*-1,5,2,4,6,8-*dithiatetrazocine* (**1**).—(*i*) *With hydrazine*. To a stirred solution of 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine (**1**) (42 mg, 0.14 mmol) in dichloromethane (15 ml) at room temperature under nitrogen was added a solution of anhydrous hydrazine (14 mg, 0.42 mmol) in dichloromethane (2 ml). After 1 h, 10% palladium on charcoal (49 mg) was added and the reaction mixture was stirred at room temperature for 3 h. It was then filtered and the filtrate evaporated. The residue was chromatographed on silica. Elution with light petroleum gave sulphur (6 mg, 65%) and with methanol, benzamidine (25 mg, 75%) was obtained.

(*ii*) *With ozone*. Ozone was passed through a stirred slurry of 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine (**1**) (55 mg, 0.2 mmol) in dichloromethane (15 ml) at −78 °C for 30 min. On warming to room temperature, the orange-yellow reaction mixture turned pale yellow and was further stirred at room temperature for 15 h. The mixture was then evaporated and the residue chromatographed on silica. Elution with ether gave 1-hydroxy-3,5-diphenyl-1,2,4,6-thiatriazine (**8**) (16 mg, 32%), identical with the earlier specimen, and with ethyl acetate, 3,5-diphenyl-1,2,4,6-thiatriazine 1,1,-dioxide (1.6 mg, 3%), identical with the earlier specimen, was obtained.

The above reaction was repeated with the ozone being passed through for 1 h at −70 °C; hydroxythiatriazine (**8**) (38%) and the thiatriazine 1,1-dioxide (5%) were obtained.

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References

1 Part 10, P. J. Dunn and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1989, preceding paper.
2 I. Ernest, W. Holick, G. Rihs, D. Schomburg, G. Shoham, D. Wenkert, and R. B. Woodward, *J. Am. Chem. Soc.*, 1981, **103**, 1540.
3 R. Gleiter, R. Bartetzko, and D. Cremer, *J. Am. Chem. Soc.*, 1984, **106**, 3437; see also J. P. Boutique, J. Riga, J. J. Verbist, J. Delhalle, J. G. Fripiat, R. C. Haddon, and M. L. Kaplan, *ibid.*, p. 312, and R. T. Oakley, *Can. J. Chem.*, 1984, **62**, 2763.
4 G. G. Alange, A. J. Banister, B. Bell, and P. W. Millen, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1192; A. J. Banister, N. R. M. Smith, and R. G. Hey, *ibid.*, 1983, 1181.
5 H. W. Roesky and T. Müller, *Chem. Ber.*, 1978, **111**, 2960.
6 'Gmelin Handbook of Inorganic Chemistry,' 8th edn., Sulfur-Nitrogen Compounds, Part 2, Springer-Verlag, Berlin, 1985, p. 203.
7 D. N. Harpp, K. Steliou, and T. H. Chan, *J. Am. Chem. Soc.*, 1978, **100**, 1222; M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2591.
8 M. Davis, *Adv. Heterocycl. Chem.*, 1982, **30**, 47.
9 E. J. Corey, B. Samuelsson, and F. A. Luzzio, *J. Am. Chem. Soc.*, 1984, **106**, 3682.
10 R. T. Boeré, A. W. Cordes, R. T. Oakley, and R. W. Reed, *J. Am. Chem. Soc.*, 1987, **109**, 868.
11 T. Chivers, J. F. Richardson, and N. R. M. Smith, *Inorg. Chem.*, 1986, **25**, 47.
12 S. T. A. K. Daley and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 203.
13 A. R. Sanger, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 351.
14 K. T. Potts, *J. Chem. Soc.*, 1954, 3461.
15 A. Pinner, *Ber.*, 1892, **25**, 1414.
16 W. Jarre, D. Bieniek, and F. Korte, *Tetrahedron*, 1975, **31**, 619.
17 S. Gronowitz and S. Liljefors, *Acta Chem. Scand., Ser. B*, 1977, **31**, 771.

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