A New Route to 1,3,4-Thiadiazolines.† Part 3.[1] Consequences of the Aza-enamine Concept

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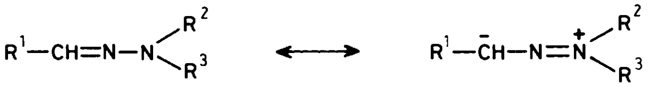
N,N-Disubstituted hydrazones react with sulphenyl chlorides, sulphur dichloride, and disulphur dichloride to give *C*-sulphenyl products. *N,N*-Tetramethylenehydrazones with SCl_2 or S_2Cl_2 give the novel pyrrolo[2,1-*b*]-1,3,4-thiadiazole ring system. Studies of the site selectivity in reactions of these hydrazones with sulphur(II) electrophiles by the semiempirical CNDO and MNDO methods are reported.

The synthetic potential of the reactions of sulphur dichloride, disulphur dichloride, and sulphenyl chlorides with unsaturated compounds is well known.[2,3] Hitherto the reactions of azomethines with these sulphur chlorides have given only *N*-sulphenyl compounds. We were interested in finding a class of compounds containing a carbon–nitrogen double bond which could be attacked by electrophiles at the carbon atom. The aza-enamine concept[4] seemed to indicate that electrophilic substitution by sulphur might occur at C-1 of an *N,N*-dialkylhydrazone. Aldehyde hydrazones are known to react with electrophiles such as halogens,[5] diazonium salts,[6] and the Vilsmeyer reagent[4] at C-1. The mesomeric structure (**II**) was claimed[4] to be responsible for this inverse reactivity.

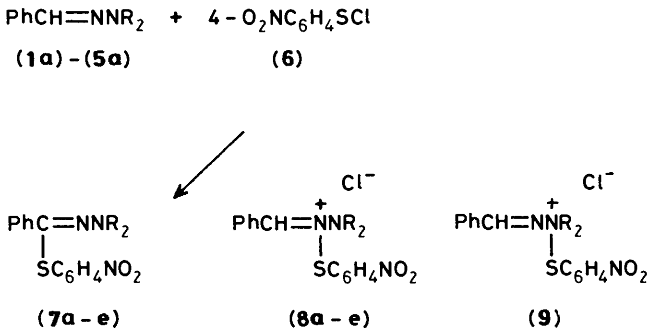


(I) (II)

Our first task was to examine the effect of the *N*-alkyl substituents on this phenomenon.

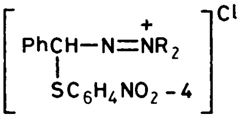
Results and Discussion

Reaction with an Arenesulphenyl Chloride.—*p*-Nitrobenzenesulphenyl chloride (**6**) was treated with the benzaldehyde *N,N*-dialkylhydrazones (**1a**)—(**5a**) (1 mol equiv.) in dichloromethane at room temperature. Since there are three nucleophilic centres in these hydrazones, one might expect the formation of *C*-sulphenyl (**7**) and *N*-sulphenyl products [(**8**) and/or (**9**)]. The ^1H n.m.r. spectra of the crude product showed a mixture of two components, which were separated by selective dissolution and recrystallization. The ether-soluble product was identified as the *C*-sulphenyl derivative (**7**). ^1H N.m.r. data indicated that the remaining ether-insoluble salt should have structure (**8**). The *CH*=N singlet appeared at δ 9.41—9.59, typical of azomethines and hydrazones protonated at the nitrogen of the azomethine bond.[5]



(7)/(8)		R	R	Product ratio (7)/(8)(%)	Yield of (7) + (8)
(1a)	a	$-[CH_2]_4-$		2.50	77
(2a)	b	$-[CH_2]_5-$		0.62	95
(3a)	c	$-[CH_2]_6-$		2.51	95
(4a)	d	Me	Me	0.46	88
(5a)	e	C_6H_{11}	C_6H_{11}	3.43	89

The formation of the product (**7**) can be understood in terms of an addition–elimination mechanism with an intermediate diazenium salt (**10**).



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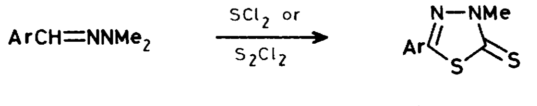

(4a-d) (11a-d)

Ar: a; Ph b; 4-$O_2NC_6H_4$ c; 2-$O_2NC_6H_4$ d; 4-ClC_6H_4

Reactions with Sulphur Dichloride and Disulphur Dichloride.—As previously reported,[7] *N,N*-dimethylhydrazones of aromatic aldehydes (**4a**—**d**) and sulphur dichloride or disulphur dichloride gave 5-alkyl-3-methyl-1,3,4-thiadiazole-2(3*H*)-thiones (**11a**—**d**). This unexpected result prompted us to study the reaction of further hydrazones with the bifunctional SCl_2 and S_2Cl_2. The *N,N*-tetramethylenehydrazones (**1a**—**e**) were treated with equimolar amounts of SCl_2 in dry dichloromethane for 1 h at −50 °C and for 24 h at room temperature. Work-up in the usual way gave a crude product, which upon recrystallization

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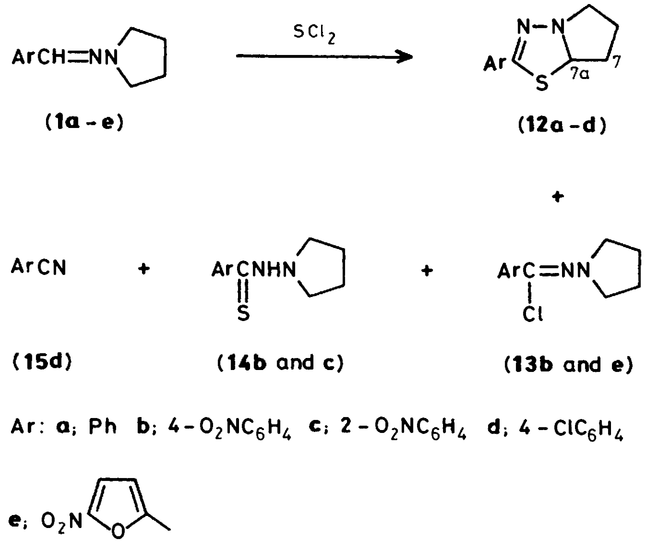
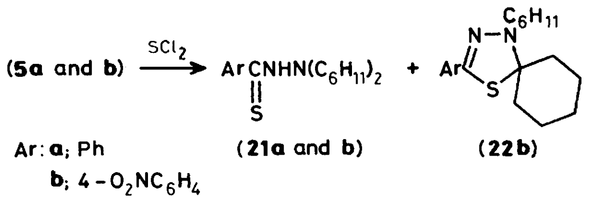
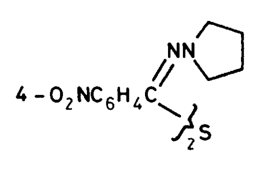
† Dihydro-1,3,4-thiadiazoles.







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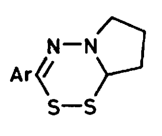

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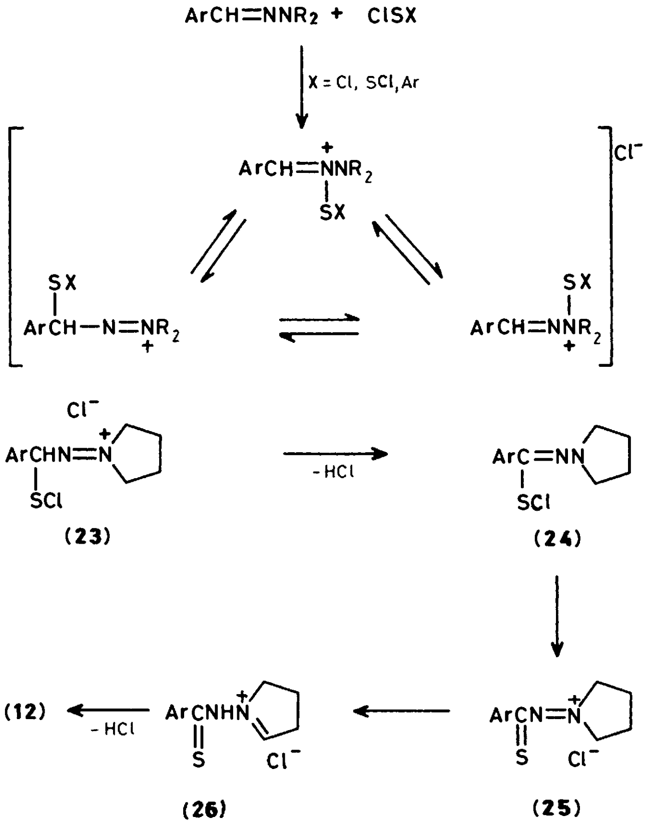
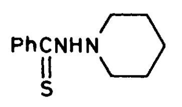


Scheme.



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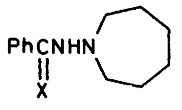


(19) X = O
(20) X = S

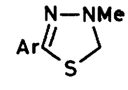
gave the novel pyrrolo[2,1-*b*]-1,3,4-thiadiazoles (**12a**—**d**). Column chromatography over silica gel yielded, as side products, the α-chloro-hydrazone (**13b**) (5%), the thiohydrazides (**14b** and **c**) (1.5 and 6%), and the nitrile (**15d**) (15%). In the reaction of 5-nitro-2-furaldehyde *N*,*N*-tetramethylenehydrazone (**1e**) with SCl_2, the α-chloro-hydrazone (**13e**) was obtained as the only product in 53% yield.

The products (**12a**—**d**) were identified on the basis of ^1H and ^{13}C n.m.r. and mass spectral data. The coupling constant $^1J_{C(7a)H} = 143$ Hz and the difference in the chemical shift of H-7a between the protonated and the unprotonated pyrrolothiadiazole (**12b**) (0.6 p.p.m.) point to an antiperiplanar arrangement of the lone pair on N-4 and the proton on the adjacent carbon atom C-7a.[8,9] Vicinal coupling constants $^3J_{7a\text{-H},7\text{-H}} =$ 6 Hz gave further evidence for *cis*-fused five-membered rings in the main conformer of (**12b**).

The reaction of (**1b**) with an equimolar amount of S_2Cl_2 at room temperature afforded the same pyrrolothiadiazole (**12b**) in higher yield (60%). Mass and ^1H n.m.r. spectra of the crude product provided no evidence for the formation of the corresponding 1,2,4,5-dithiadiazine (**16**). The reaction of (**1b**) with SCl_2 or S_2Cl_2 is accompanied by elimination of hydrogen chloride. In order to achieve higher product yields, the reaction of (**1b**) with SCl_2 was carried out in the presence of triethylamine. The 2:1 insertion product (**17**) was detected and isolated as the only product. No product was observed when the *N*,*N*-pentamethylenehydrazones (**2a** and **b**) were treated with SCl_2. Only after addition of triethylamine could the thiohydrazide (**18**) be separated (in 23% yield), mainly from unchanged starting material. The *N*,*N*-hexamethylenehydrazone (**3a**) and SCl_2 gave a crude product which was washed with aqueous sodium hydrogen carbonate and separated over silica gel to give the hydrazide (**19**) (20%) and the thiohydrazide (**20**) (20%).

The thiohydrazides (**21a** and **b**) were obtained from the *N*,*N*-dicyclohexylhydrazones (**5a** and **b**) and SCl_2 only in the presence of Et_3N. In the case of the *p*-nitro derivative, a further product was isolated, exhibiting ^1H n.m.r. and mass spectra in good agreement with the structure of the cyclization product (**22**).

The formation of the thiadiazole ring from hydrazones and SCl_2 can be explained in terms of five consecutive reactions (Scheme). The first step comprises electrophilic attack by SCl_2 on the azomethine carbon, producing the diazenium salt (**23**) which is stabilized in the second step by elimination of hydrogen chloride. Postulation of compound (**24**) as an intermediate seems



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reasonable in view of the formation of the *C*-sulphenyl derivative (**7**) from (**1a**)—(**5a**) and *p*-nitrobenzenesulphenyl chloride as well as the isolation of the 2:1 insertion product (**17**). Rearrangement of (**24**) to the thioacyldiazenium salt (**25**) should be strongly influenced by the substituent in the aromatic ring. Electron-withdrawing groups and enhancement of delocalization will lower the activation energy as suggested for the *p*-nitrophenyl in comparison with the phenyl derivative. Prototropy and electrocyclization to thiadiazoles is well known in the chemistry of thioacyl-*N*,*N*-dialkylhydrazones.[10] Involvement of the pyrrolidine moiety in electrocyclization reactions ('tert-amino effect') is also well documented.[11]

The expected thiazoline (**27**) was not observed in reactions with *N*,*N*-dimethylhydrazones, probably because of fast reaction of a further equivalent of SCl_2 with the acidic methylene group[12] and formation of (**11**).

The occurrence of α-chloro-hydrazones in the reaction mixture can be explained if one takes into account that SCl_2 exists as an equilibrium mixture of SCl_2, S_2Cl_2, and Cl_2 containing 3% free Cl_2 at -50 °C.[13]

Theoretical Considerations.—Enamines are ambident conjugated systems with high nucleophilicity at both the nitrogen and the β-carbon atom. Site preference for electrophilic attack depends on both the nature of the enamine and the electrophile. Thus, careful differentiation between thermodynamic and kinetic control is necessary, but often difficult.[14] Further complications arise in the enamine-like 'tridentate' hydrazones, from the additional nitrogen electron lone pair. In contrast to the yields of thiadiazoles from the hydrazones (**1**)—(**5**) with SCl_2, the product ratio (**7**)/(**8**) shows that dicyclohexylamino, hexamethyleneamino, and tetramethyleneamino are strong, and pentamethyleneamino and dimethylamino are weak electron-donating substituents with respect to the azomethine carbon atom. To explain these product ratios we calculated the net electron densities (δ_T) and the electron densities in the p_z atomic orbital (δ_p) for the C=N–N moiety by the CNDO/2 method.[15] No significant charge differences were observed for the hydrazones (**1a**), (**1b**), (**3a**), (**4a**), and (**4b**). Because of the slightly negatively charged nitrogen atoms, the differences in δ_T vary between $+0.052$ (**4b**) and $+0.037$ (**3a**) and in δ_p from -0.07 (**4b**) to -0.025 (**3a**) at the carbon atom.

Our second task was to examine the energy gain which arises from the overlap of the p atomic orbitals of the occupied hydrazone molecular orbitals with the LUMO (α) of SCl_2 using Fukui's superdelocalization term[16] [equation (i)]. The eigenvalues (ε_i) and atomic coefficients (c_i) were obtained by the CNDO/S[17] method. Resonance integrals were calculated for a distance of 0.3 nm[18] for the two reactive centres in the transition state as follows: $\beta_{C-S} = 1.5726$; $\beta_{N-S} = 1.0716$. The results for electrophilic attack of sulphur dichloride perpendicular to the plane of the hydrazone are listed in Table 1.

$$S_r^{(E)} = -2 \sum_i^{\mathrm{occ}} \frac{c_i^2}{\alpha - \varepsilon_i} \beta \qquad \text{(i)}$$

Table 1. Superdelocalization indexes ($S_r^{(E)} \times 10^2$)

Hydrazone	C	N	N
(**1a**)	10.27	6.57	12.78
(**1b**)	9.43	6.81	12.54
(**3a**)	9.47	5.38	11.60
(**4a**)	6.71	7.81	12.07
(**4b**)	9.56	7.81	11.19

Table 2. Calculated torsion angles and bond lengths

Hydrazone	α/°	β/°	*d*(C=N)/nm	*d*(N–N)/nm
(**1a**)	2.1	6.0	0.131 003	0.132 340
(**4a**)	15.3	19.5	0.130 324	0.134 069
(**4b**)	11.9	16.7	0.130 652	0.133 566
(**4d**)	18.3	18.2	0.130 698	0.134 092

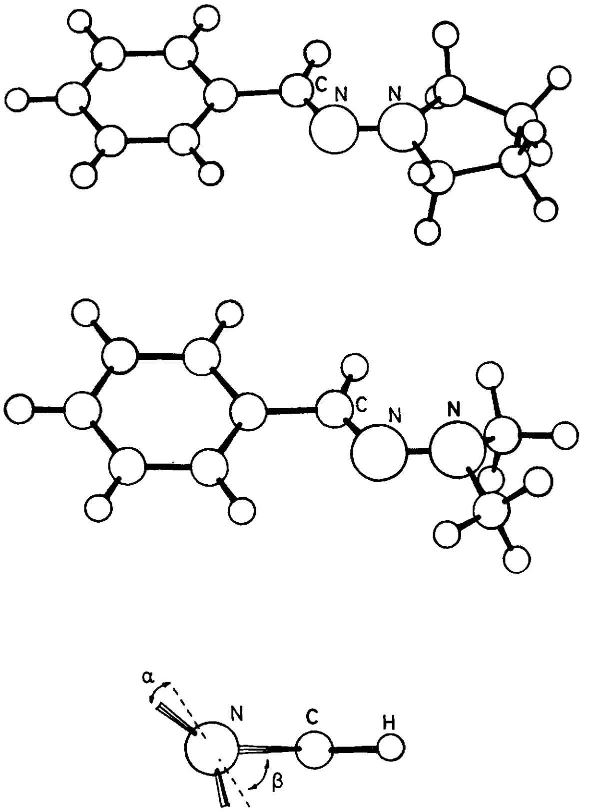

Figure. ORTEP drawing of calculated equilibrium configurations of the hydrazones (**4a**) and (**1a**); designation of torsion angles α and β

These $S_r^{(E)}$ indexes show clearly that electrophilic attack on the amine nitrogen is favoured kinetically. The deviation from planarity (*i.e.* from ideal sp^2 hybridization[19]) at the disubstituted amine nitrogen atom has been used as an argument for explaining the decreasing reactivity of enamines. Therefore, we performed a full geometry optimization of the hydrazones (**1a**), (**4a**), (**4b**), and (**4d**) by the MNDO method.[20] Some structural aspects of the equilibrium configurations are characteristic. With the exception of the amine residue the molecule remains nearly planar, with shortened nitrogen–nitrogen single bonds and lengthened azomethine carbon–nitrogen double bonds (Table 2). This can be understood by inclusion of the polar mesomeric hydrazone structure (**II**). Pyramidalization at the nitrogen atom is coupled with torsion around the N–N bond so that the *N*-substituent *syn* to the C=N double bond is moved more out of the C=N–N plane than the other one (see Figure).

A near planar structure and hence an sp^2-type amine nitrogen is achieved in benzaldehyde *N*,*N*-tetramethylenehydrazone

(**1a**) in contrast with the *N,N*-dimethylhydrazones (**4**) with a nearly tetrahedral sp^3-type nitrogen. These results are in good agreement with the product ratios (**7**)/(**8**), but not with those for the reaction with SCl_2, especially with respect to the effect of the *para*-substituents. Surprisingly, both the *p*-nitro and the *p*-chloro substituent have only a minor influence on nitrogen pyramidalization, although large differences in reactivity were observed.

In view of the foregoing experimental and theoretical data, we propose, in contradiction to the azaenamine concept, that initial attack by sulphur occurs at the nitrogen atoms. Rearrangement to the *C*-sulphenyl diazenium salt then allows elimination of hydrogen chloride, by stabilizing the system. Electron-withdrawing substituents in the aromatic ring should markedly favour this stabilization. To obtain support for this argument, the reaction of (**1a**) with (**6**) was repeated in a ^1H n.m.r. tube. Shortly after addition of (**6**) to (**1a**) in $CDCl_3$ the only signals observed were due to (**8**); these signals decayed slowly to give after some days the spectrum of (**7**) only. The isolated salt (**8a**) slowly rearranges in solution to (**7**).

Experimental

M.p.s were determined with a Boetius apparatus and are corrected. Products were separated on a silica gel medium-pressure column (Merck Lobar-Fertigsäule B). I.r. spectra were taken with a UR 20 spectrophotometer (Carl-Zeiss Jena) for KBr discs. Mass spectra were recorded with a Varian-Mat CH6 instrument. ^1H N.m.r. spectra were obtained with a Tesla BS 487 C instrument, and ^{13}C n.m.r. spectra with a JEOL JNM-FX 100 instrument, with deuteriochloroform as solvent and tetramethylsilane as internal standard. Microanalyses were performed by the microanalytical laboratory, Karl-Marx-Universität.

Table 3. Data for the products (**7**) and (**8**)

Compd.	Yield (%)	M.p. (°C)	m/z^a
(**7a**)	55	92.5—94	327
(**8a**)	22	135—137	328
(**7b**)	36	88—91	341
(**8b**)	59	155—158	342
(**7c**)	68	85.5—87	355
(**8c**)	27	138—145	356
(**7d**)	28	75—77	301
(**8d**)	60	162—172	302
(**7e**)	69	(Red oil)	437
(**8e**)	20	126	438

[a] In the case of compound (**7**) M^+, in the case of (**8**) $M^+ - Cl$.

Reactions with 4-Nitrobenzenesulphenyl Chloride (*General Method A*).—A solution of *p*-nitrobenzenesulphenyl chloride (**6**) (0.95 g, 5 mmol) in methylene dichloride (15 ml) was added rapidly to a solution of the appropriate hydrazone (5 mmol) in methylene dichloride. The mixture was stirred for 48 h at room temperature, then evaporated. The residue was triturated with ether (50 ml), filtered off, and washed with ethanol. Purification, by evaporation of the filtrate, trituration with ether, and washing the obtained benzaldehyde N^2,N^2-dialkyl-N^1-(4-nitrophenylthio)hydrazonium chlorides (**8a**—**e**) (Table 3) with ethanol was repeated several times.

Benzaldehyde N^1-(4-nitrophenylthio)-N^2,N^2-tetramethylenehydrazonium chloride (**8a**) showed δ_H 2.18—2.43 (4 H, m, CH_2), 3.43—3.91 (4 H, m, CH_2), 7.38—7.89 (9 H, m, Ph and ArH), and 9.41 (1 H, s, CH).

The N^2,N^2-pentamethylene derivative (**8b**) showed δ_H 1.53—1.91 (2 H, m, CH_2), 1.99—2.39 (4 H, m, CH_2), 3.26—3.61 (4 H, m, CH_2), 7.31—8.31 (9 H, m, Ph and ArH), and 9.59 (1 H, s, CH). The N^2,N^2-hexamethylene derivative (**8c**) showed δ_H 1.68—1.93 (4 H, m, CH_2), 1.98—2.31 (4 H, m, CH_2), 3.43—3.68 (4 H, m, CH_2), 7.43—7.88 (9 H, m, Ph and ArH), and 9.51 (1 H, s, CH). The N^2,N^2-dimethyl derivative (**8d**) showed δ_H 3.30 (6 H, s, CH_3), 7.25—8.62 (9 H, m, Ph and ArH), and 9.50 (1 H, s, CH). The N^2,N^2-dicyclohexyl derivative (**8e**) showed δ_H 1.00—2.56 (20 H, m, CH_2), 3.38—3.86 (2 H, m, NCH), 7.38—7.66 (5 H, m, Ph and ArH), 7.81—7.98 (4 H, m, Ph and ArH), and 9.49 (1 H, s, CH).

The residues, recrystallized from ethanol, yielded the following benzaldehyde *N,N*-dialkyl-α-(4-nitrophenylthio)hydrazones (**7a**—**e**) (Table 3): *N,N*-tetramethylene- (**7a**), δ_H 1.51—2.16 (4 H, m, CH_2), 3.18—3.81 (4 H, m, CH_2), and 6.93—8.03 (9 H, m, Ph and ArH); *N,N*-pentamethylene- (**7b**), δ_H 1.39—1.94 (6 H, m, CH_2), 3.04—3.11 (4 H, m, CH_2), 7.11—7.56 (5 H, m, Ph), and 7.29 and 7.94 (4 H, d, *J* 9 Hz, ArH); *N,N*-hexamethylene- (**7c**), δ_H 1.43—1.93 (8 H, m, CH_2), 3.43—3.63 (4 H, m, CH_2), 7.13—7.36 (5 H, m, Ph and ArH), 7.56—8.53 (2 H, m, Ph and ArH), and 8.00 (2 H, d, *J* 9 Hz, ArH); *N,N*-dimethyl- (**7d**), δ_H 2.17 (6 H, s, CH_3), 7.11—7.44 (5 H, m, Ph), and 7.26 and 7.91 (4 H, d, *J* 9 Hz, ArH); *N,N*-dicyclohexyl- (**7e**), δ_H 0.99—1.98 (20 H, m, CH_2), 3.31—3.71 (2 H, m, CH), 7.11—7.73 (5 H, m, Ph), and 7.17 and 7.92 (4 H, d, *J* 9 Hz, ArH).

Reactions with Sulphur Dichloride (*General Method B*).—To a stirred solution of sulphur dichloride (4.12 g, 40 mmol) in dry methylene dichloride a solution of the appropriate hydrazone (40 mmol) was added over 20 min at −50 °C. After 1 h the solution was allowed to warm to room temperature, and after 2 days the mixture was washed with aqueous sodium hydrogen carbonate and water, and evaporated to dryness.

Reactions of N,N-*Tetramethylenehydrazones* (**1a**—**e**) *with Sulphur Dichloride*.—By the general method B, the following

Table 4. Data for products (**12**)—(**15**)

Compd.	Yield (%)	M.p. (°C)	m/z (M^+)	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
(**12a**)	13	49—53	204	64.6	6.0	13.7	16.0	$C_{11}H_{12}N_2S$	64.7	5.9	13.7	15.7
(**12b**)	48	95—98	249	52.8	4.7	16.1	12.2	$C_{11}H_{11}N_3O_2S$	53.0	4.45	16.9	12.9
(**13b**)	5	74—76	253	51.8	5.1	16.2		$C_{11}H_{12}ClN_3O_2$	52.1	4.8	16.6	
(**14b**)	1.5	109—113	251	52.7	5.8		12.7	$C_{11}H_{13}N_3O_2S$	52.6	5.2		12.7
(**12c**)	18	(Red oil)	249	53.25	4.75	16.9	13.0	$C_{11}H_{11}N_3O_2S$	53.0	4.45	16.9	12.9
(**14c**)	6	98—106	251	52.9	5.0	16.5	12.6	$C_{11}H_{13}N_3O_2S$	52.6	5.2	16.7	12.8
(**12d**)	13	(Red oil)	238	55.2	4.8	11.6	13.7	$C_{11}H_{11}ClN_2S$	55.3	4.7	11.7	13.4
(**15d**)	15	95—99	137					C_7H_4ClN				
(**13e**)	53	67—68.5	243	44.2	4.0	17.1		$C_9H_{10}ClN_3O_3$	44.4	4.1	17.25	14.55

5,6,7,7a-tetrahydropyrrolo[2,1-*b*]-1,3,4-thiadiazoles (**12a**—**d**), α-chloro-hydrazones (**13b** and **e**), thiohydrazides (**14b** and **c**), and nitrile (**15d**) were prepared; they were separated by column chromatography with n-hexane–acetone (8:2) as eluant (Table 4).

2-*Phenyl*-5,6,7,7a-*tetrahydropyrrolo*[2,1-b]-1,3,4-*thiadiazole* (**12a**), δ_H 1.55—2.29 (4 H, m, CH_2), 3.08—3.95 (2 H, m, CH_2), 5.14 (1 H, t, *J* 6 Hz, CH), and 7.14—7.64 (5 H, m, Ph); δ_C 22.7 (t, C-6), 35.3 (t, C-7), 54.3 (t, NCH_2), 73.8 (d, NCHS), 146.5 (s, C=N), 131.2 (s, C-1 of Ph), 126.9 (d, C-2 of Ph), 128.3 (d, C-3 of Ph), and 129.4 (d, C-4 of Ph); 2-(4-*nitrophenyl*)- (**12b**), δ_H 1.56—2.30 (4 H, m, CH_2), 3.30—4.06 (2 H, m, CH_2), 5.26 (1 H, t, *J* 6 Hz, CH), and 7.85 and 8.21 (4 H, d, *J* 9 Hz, ArH); δ_C 22.6 (t, C-6), 35.4 (t, C-7), 54.2 (t, NCH_2), 74.8 (d, NCHS), 144.1 (s, C=N), 137.4 (s, C-1 of Ar), 127.6 (d, C-2 of Ar), 123.7 (d, C-3 of Ar), and 147.9 (s, C-4 of Ar); 2-(2-*nitrophenyl*)- (**12c**), δ_H 1.56—2.31 (4 H, m, CH_2), 3.36—3.74 (2 H, m, NCH_2), 5.25 (1 H, t, *J* 7 Hz, CH), and 7.12 and 7.85 (4 H, m, ArH); δ_C 22.8 (t, C-6), 35.2 (t, C-7), 54.2 (t, NCH_2), 75.6 (d, NCHS), 141.7 (s, C=N), and 125.7, 148.5, 130.1, 124.1, 132.4, and 130.8 (Ar); 2-(4-*chlorophenyl*)- (**12d**), δ_H 1.56—2.24 (4 H, m, CH_2), 3.19—3.94 (2 H, m, CH_2), 5.17 (1 H, t, *J* 7 Hz, CH), and 7.27 and 7.55 (4 H, d, *J* 8 Hz, ArH).

α-*Chloro*-4-*nitrobenzaldehyde* N,N-*tetramethylenehydrazone* (**13b**), δ_H 1.84—2.08 (4 H, m, CH_2), 3.50—3.81 (4 H, m, CH_2), and 8.17 and 7.96 (4 H, d, *J* 9 Hz, ArH); $\nu_{max.}$ 1 560 (C=N), 1 520, and 1 340 cm^{-1} (NO_2).

α-*Chloro*-5-*nitro*-2-*furaldehyde* N,N-*tetramethylenehydrazone* (**13e**), δ_H 1.84—2.06 (4 H, m, CH_2), 3.56—3.81 (4 H, m, CH_2), and 6.74 and 7.35 (2 H, d, *J* 4 Hz, ArH); $\nu_{max.}$ 1 560 (C=N), and 1 490 and 1 290 cm^{-1} (NO_2).

4-*Nitro*-NN-*tetramethylenebenzothiohydrazide* (**14b**), δ_H 2.05—2.25 (4 H, m, CH_2), 3.81—4.04 (4 H, m, CH_2), 8.28 (4 H, s, ArH), and 10.90 (1 H, s, NH); $\nu_{max.}$ 1 520 (NO_2), 1 470, and 1 320 cm^{-1} (S=C–N).

2-*Nitro*-N,N-*tetramethylenebenzothiohydrazide* (**14c**), δ_H 2.09—2.36 (4 H, m, CH_2), 3.38—3.68 (4 H, m, CH_2), 7.18—7.86 (4 H, m, ArH), and 11.31 (1 H, s, NH); $\nu_{max.}$ 1 530 and 1 350 (NO_2), and 1 460 and 1 300 cm^{-1} (S=C–N).

4-Chlorobenzonitrile (**15d**), $\nu_{max.}$ 2 240 (C≡N).

Reaction of the Hydrazone (**1b**) *with Disulphur Dichloride.*—To a stirred solution of disulphur dichloride (5.54 g, 40 mmol) in methylene dichloride was added, a solution of (**1b**) (8.76 g, 40 mmol) in methylene dichloride, and the mixture was stirred at room temperature for 1 day. Evaporation of the solvent and recrystallization of the crude product from ethanol yielded the pyrrolothiadiazole (**12b**) (5.98 g, 60%).

Reaction of the Hydrazone (**1b**) *with Sulphur Dichloride and Triethylamine.*—To a stirred solution of sulphur dichloride (1.8 g, 17 mmol) in methylene dichloride was added, a solution of (**1b**) (3.3 g, 15 mmol) and triethylamine (3.03 g, 30 mmol) in methylene dichloride at −50 °C. After 1 h the mixture was allowed to warm to room temperature, and after 7 h the solvent was evaporated off. Crystallization from ethanol yielded *bis*-[4-*nitro*-α-(N,N-*tetramethylenehydrazono*)*benzyl*] *sulphide* (**17**) (1.2 g, 34%), m.p. 165—174 °C (from EtOH), m.p. 180—185 °C [from acetone–water (10:1)] (Found: C, 56.4; H, 5.2; N, 17.9; S, 6.9. $C_{22}H_{24}N_6O_4S$ requires C, 56.1; H, 5.2; N, 18.2; S, 6.8%); *m/z* 468 (M^+); $\nu_{max.}$ 1 540 (C=N), and 1 520 and 1 325 cm^{-1} (NO_2); δ_H 1.86—2.06 (8 H, m, CH_2), 3.66—3.44 (8 H, m, CH_2), and 7.40 and 7.91 (8 H, d, *J* 9 Hz, ArH); δ_C 24.4 (CH_2), 57.0 (NCH_2), 123 (C-3 and -5 of Ar), 127.5 (C-2 and -6 of Ar), 134.4 (C-1 of Ar), 144.6 (C=N), and 147.0 (C-4 of Ar).

Reactions of the N,N-*Penta- and* N,N-*Hexa-methylenehydrazones* (**2**) *and* (**3**) *and of the* N,N-*Dicyclohexylhydrazones* (**5**) *with Sulphur Dichloride.*—General method B was modified, by adding triethylamine (4.04 g, 40 mmol) to the reaction mixture when it was allowed to warm to room temperature. The thiohydrazides (**18**), (**20**), (**21a**), and (**21b**), the hydrazide (**19**), and the thiadiazole (**22**) were separated by column chromatography with n-hexane–acetone (20:7) as eluant. *N*,*N*-Pentamethylenebenzothiohydrazide (2.03 g, 23%) (**18**) was a yellow oil; *m/z* 220 (M^+); δ_H 1.41—2.19 (6 H, m, CH_2), 3.06—3.56 (4 H, m, CH_2), 7.14—7.44 (3 H, m, Ph), 7.86—8.19 (2 H, m, Ph), and 11.40 (1 H, s, NH); $\nu_{max.}$ 3 400 (NH), 1 460, and 1 220 cm^{-1} (S=C–N). *N*,*N*-Hexamethylenebenzohydrazide (1.75 g, 20%) (**19**) was a brown oil; *m/z* 218 (M^+); δ_H 1.46—1.93 (8 H, m, CH_2), 3.06—3.31 (4 H, m, CH_2), 7.18—7.53 (3 H, m, Ph), and 7.68—7.81 (2 H, m, Ph); $\nu_{max.}$ 3 450 (NH), 1 550, and 1 300 cm^{-1} (O=C–N). *N*,*N*-Hexamethylenebenzothiohydrazide (1.84 g, 20%) (**20**) had m.p. 65—68 °C; *m/z* 234 (M^+); δ_H 1.71—2.19 (8 H, m, CH_2), 3.29—3.54 (4 H, m, CH_2), 7.24—7.44 (3 H, m, Ph), 7.94—8.12 (2 H, m, Ph), and 11.60 (1 H, s, NH); $\nu_{max.}$ 3 450 (NH), 1 450, and 1 330 cm^{-1} (S=C–N). N,N-*Dicyclohexylbenzothiohydrazide* (1.90 g, 15%) (**21a**) had m.p. 150—158 °C (from ethanol) (Found: C, 72.45; H, 8.5; N, 9.3; S, 9.6. $C_{19}H_{28}N_2S$ requires C, 72.1; H, 8.9; N, 8.85; S, 10.1%); *m/z* 316 (M^+); δ_H 1.06—2.56 (20 H, m, CH_2), 3.19—3.76 (H, m, NCH), 7.08—7.38 (3 H, m, Ph), 7.95—8.18 (2 H, m, Ph), and 11.41 (1 H, s, NH); $\nu_{max.}$ 3 450 (NH), 1 450, and 1 340 cm^{-1} (S=C–N). N,N-*Dicyclohexyl*-4-*nitrobenzothiohydrazide* (2.90 g, 20%) (**21b**) had m.p. 132—134 °C (Found: C, 62.65; H, 7.3; N, 11.5; S, 9.05. $C_{19}H_{27}N_3O_2S$ requires C, 63.1; H, 7.5; N, 11.6; S, 8.9%); *m/z* 361 (M^+); δ_H 1.00—2.30 (20 H, m, CH_2), 3.73—3.25 (1 H, m, NCH), 8.16 (4 H, s, ArH), and 11.08 (1 H, s, NH); $\nu_{max.}$ 3 450 (NH), 1 520 (NO_2), 1 440 and 1 340 (S=C–N), and 1 320 cm^{-1} (NO_2). 3′-*Cyclohexyl*-5′-(4-*nitrophenyl*)*spiro*{cyclohexane-1,2′(3′H)-[1,3,4]*thiadiazole*} (3.02 g, 21%) (**22**) had m.p. 199—203 °C (Found: C, 63.6; H, 7.0; N, 12.0; S, 9.3. $C_{19}H_{25}N_3O_2S$ requires C, 63.5; H, 7.0; N, 11.7; S, 8.9%); *m/z* 359 (M^+); δ_H 1.07—2.36 (20 H, m, CH_2), 3.74—4.19 (1 H, m, NCH), and 8.31 and 8.61 (4 H, d, *J* 8.5 Hz, ArH); $\nu_{max.}$ 1 580 (C=N) and 1 350 cm^{-1} (NO_2).

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