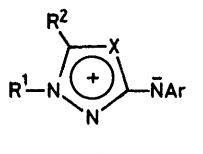
Cyclic Meso-ionic Compounds. Part 15.[1a] Synthesis, Spectroscopic Properties, and Chemistry of 1,3,4-Thiadiazolium-2-benzylidenehydrazinides and 1,2,4-Triazolium-3-benzylidenehydrazinides [1b,†]

By Eric Cawkill, W. David Ollis,* Christopher A. Ramsden, and Graham P. Rowson, Department of Chemistry, The University, Sheffield S3 7HF

The preparation of 1,3,4-thiadiazolium-2-benzylidenehydrazinides (8) and 1,2,4-triazolium-3-benzylidenehydrazinides (10), two novel types of meso-ionic heterocycle, is described. In aqueous ethanolic ammonia solution, rearrangement of the meso-ionic compound (8c) to the isomeric meso-ionic 1,2,4-triazolium-3-thiolate (18c) has been observed. The meso-ionic 1,3,4-thiadiazoles (8) yield the 1,3-dipolar cycloadducts (25) with 4-phenyl-1,2,4-triazoline-3,5-dione (24).

We have described the synthesis of the meso-ionic 1,3,4-thiadiazolium-2-aminides (1; X = S),[2] 1,2,4-triazolium-3-aminides † (1; X = NR),[3] and 1,3,4-oxadiazolium-2-aminides (1; X = O)[4] by the reaction of hydrazine derivatives (2; X = S, NR, and O) with dichloromethyleneamines (RN=CCl_2). We now report an extension of this general synthetic route to include the preparation of a new class of meso-ionic heterocycles (3) which have an extended π-electron system exocyclic to the meso-ionic ring. These meso-ionic heterocycles are synthesized by the reaction of the hydrazines (2; X = S or NR) with aryl dibromodiazabutadienes (4) and, in one case, with a trichlorodiazabutadiene (5).



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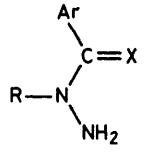

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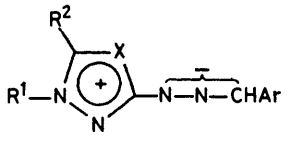

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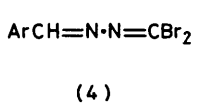

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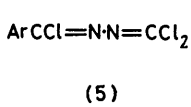

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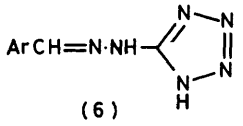

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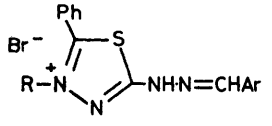

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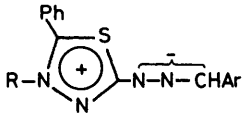

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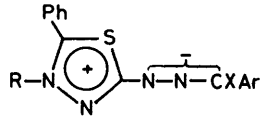


(9)

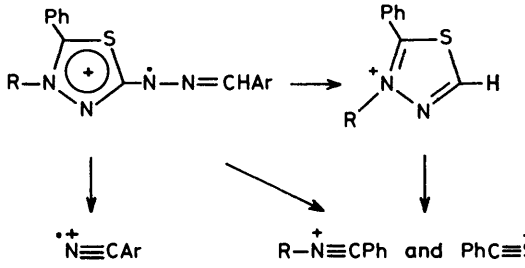
a; R = Me, Ar = Ph
b; R = Me, Ar = *p*-MeC_6H_4
c; R = Me, Ar = *p*-ClC_6H_4
d; R = Me, Ar = *p*-$MeOC_6H_4$
e; R = Ph, Ar = *p*-ClC_6H_4
f; R = Ar = Ph

The preparation of dibromodiazabutadienes (4) by bromination of 5-(benzylidenehydrazino)tetrazoles (6) has been described.[5] Using this procedure, we have prepared four derivatives (4a—d). 1,1,4-Trichloro-4-(4-chlorophenyl)-2,3-diazabuta-1,3-diene (5c) was prepared by the chlorination of 5-(4-chlorobenzylidenehydrazino)tetrazole (6c).[6] We have prepared the 5-(benzylidenehydrazino)tetrazoles (4a—d) by a modification of the general method described by Thiele and Morais[7] (see Experimental section).

When 1,1-dibromo-4-phenyl-2,3-diazabuta-1,3-diene (4a) and *N*-methyl-*N*-thiobenzoylhydrazine (2a; X = S) in equivalent proportions were dissolved in benzene and heated under reflux, the pale yellow product was identified as the 1,3,4-thiadiazolium bromide (7a). Similarly, the yellow crystalline thiadiazolium bromides (7b—e) were prepared. The i.r. spectra of compounds (7a—e) show absorptions which are characteristic of N–H stretching (3 000—2 600 cm^{-1}) and N–H bending (1 580—1 500 cm^{-1}) vibrations. An absorption at 1 600 cm^{-1} can be attributed to the arylidene (ArCH=N) stretching frequency.

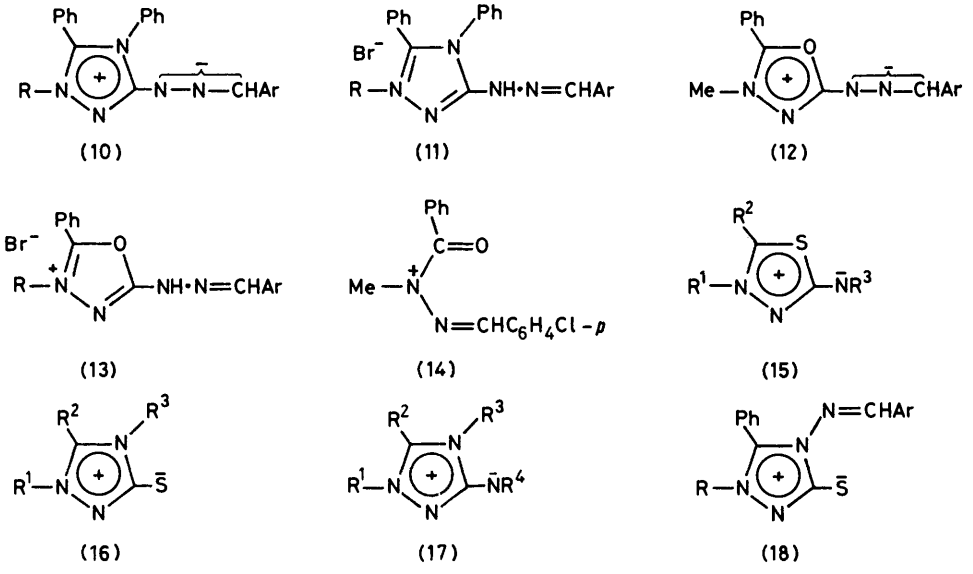
† In previous articles in this series, (*e.g.* in ref. 3), closely related compounds were named as 1,3,4-triazolium derivatives to emphasize their structural relationship to 1,3,4-thiadiazolium and 1,3,4-oxidiazolium compounds. However, they are correctly named as 1,2,4-triazolium derivatives according to I.U.P.A.C. nomenclature rules.

Treatment of the bromides (7a—e) with dry ammonia in methylene chloride gave the red crystalline meso-ionic 1,3,4-thiadiazolium-2-benzylidenehydrazinides (8a—e) in good yield. The spectroscopic properties of



SCHEME. The mass spectral fragmentation pattern of the meso-ionic 1,3,4-thiadiazolium-2-benzylidenehydrazinides (8)

the heterocycles (8a—e) support their formulation as meso-ionic compounds. The i.r. spectra show several absorption bands which can be attributed to C=N stretching vibrations (1 600—1 500 cm^{-1}). However, on the evidence available, it is not possible to make C=N assignments specifically to the exocyclic imine



R and Ar as in formulae (1)—(9)

absorption. The n.m.r. spectra show *N*-methyl signals whose chemical shifts (τ 6.1—6.2) are very similar to values previously reported for the meso-ionic thiadiazoliumaminides (1; X = S, R^1 = Me).[2] A low-field signal (τ *ca.* 1.8) can be assigned to the arylidene proton (-N=C*H*-Ar).

The compounds (8a—e) all show molecular ions in their mass spectra. Fragmentation occurs giving the 3-substituted-2-phenyl-1,3,4-thiadiazolium cation (Scheme) or the aryl cyanide radical cation ($ArC\equiv\dot{N}$). Further fragmentation gives peaks corresponding to the ions $PhC\equiv\overset{+}{S}$ (*m/e* 121) and $PhC\equiv\overset{+}{N}R$ (R = Me or Ph) characteristic of meso-ionic 1,3,4-thiadiazoles.[8]

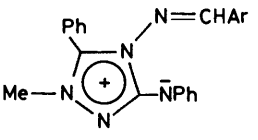
Treatment of *N*-methyl-*N*-thiobenzoylhydrazine (2a; X = S) with 1,1,4-trichloro-4-(4-chlorophenyl)-2,3-diazabuta-1,3-diene (5c) in hot benzene gave a colourless, hygroscopic chloride which, with triethylamine in methylene chloride, gave the 1,3,4-thiadiazolium-2-benzylidenehydrazinide (9c; X = Cl) as bright red crystals. This compound (9c; X = Cl) with potassium cyanide in dimethylformamide gave the cyano-compound (9c; X = CN).

We have also prepared the meso-ionic 1,2,4-triazolium-3-benzylidenehydrazinides (10) from 4-aryl-1,1-dibromo-2,3-diazabuta-1,3-dienes (4) and *N*-amino-*N*-methyl-*N'*-phenylbenzamidine (2a; X = NPh) in boiling chloroform solution. The intermediate triazolium bromides (11a—d) have i.r. spectra similar to those of the thiadiazolium bromides (7a—d). Treatment of these triazolium bromides (11a—d) with dry ammonia in methylene chloride solution gave the yellow, crystalline, meso-ionic 1,2,4-triazolium-3-benzylidenehydrazinides (10a—d).

The formulation of the heterocycles (10a—d) as meso-ionic compounds is supported by their spectroscopic properties. Their i.r. spectra show several C=N stretching absorptions and the n.m.r. spectra *N*-methyl (τ 6.1—6.2) and arylidene signals (ArC*H*-, τ 1.8—1.9). Their mass spectra can be rationalised by a fragmentation scheme corresponding to that in the Scheme. The triazoliumbenzylidenehydrazinides (10a—d) show a molecular ion and daughter ions corresponding to the structures $PhC\equiv\overset{+}{N}Ph$ (*m/e* 180) and $MeN\equiv\overset{+}{C}Ph$ (*m/e* 118).[8]

Attempts to prepare the meso-ionic 1,3,4-oxadiazolium-2-benzylidenehydrazinides (12) from *N*-benzoyl-*N*-methylhydrazine (2a; X = O) and 4-aryl-1,1-dibromo-2,3-diazabuta-1,3-dienes (4) were unsuccessful. Thus, *N*-benzoyl-*N*-methylhydrazine (2a; X = O) and the chlorophenyl compound (4c) when heated under re-

flux in methylene chloride solution did not give the expected 1,3,4-oxadiazolium bromide (13c) but instead *N*-benzoyl-*N'*-(4-chlorobenzylidene)-*N*-methylhydrazine (14) and dibromo(hydrazono)methane (H_2N–N=CBr_2) were isolated. The structure of the hydrazone (14) was established by its comparison with an authentic sample prepared from *p*-chlorobenzaldehyde and *N*-benzoyl-*N*-methylhydrazine (2a; X = O). The structure of dibromo(hydrazono)methane was confirmed by its reaction with *p*-chlorobenzaldehyde giving the 4-chlorophenyldiazabutadiene (4c).



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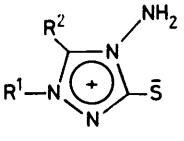

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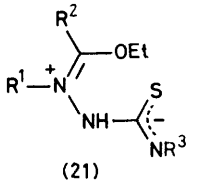

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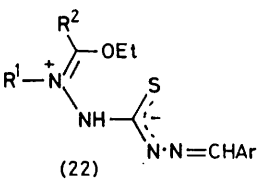

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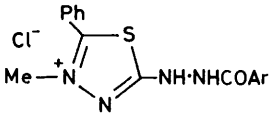

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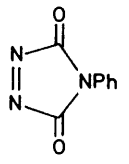

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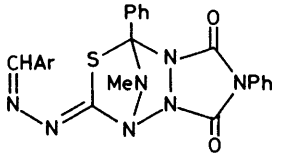


(25)

R and Ar as in formulae (1)—(18)

The meso-ionic 1,3,4-thiadiazolium-2-aminides (15) have been reported to rearrange to the meso-ionic 1,2,4-triazolium-3-thiolates (16) [2] in ethanol solution; a similar transformation has also been observed for the meso-ionic 1,2,4-triazolium-3-aminides (17).[3] We have now investigated the possibility of observing the rearrangements (8 ⟶ 18) and (10 ⟶ 19) in ethanol solution. The thiadiazoliumbenzylidenehydrazinide (8c) was unchanged in hot ethanol, but when it was heated under reflux in aqueous ethanol saturated with ammonia for 10 days, the red colour slowly faded giving a pale yellow solution. The product was a two-component mixture which was separated by t.l.c., the components of which were identified as the triazoliumthiolates (18c) and (20; R^1 = Me, R^2 = Ph). This amino-compound (20; R^1 = Me, R^2 = Ph) is probably formed by aminolysis or hydrolysis of the hydrazone (18). Clearly, a rearrangement of the general type (15 ⟶ 16) has occurred. A mechanism involving a betaine intermediate (21) has been proposed for the ethanol-catalysed rearrangements (15 ⟶ 16).[2] The rearrangement (8 ⟶ 18) may well involve a similar zwitterionic intermediate (22).

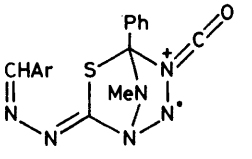
In a similar experiment, the diphenyl compound (8e) gave exclusively the hydrolysed rearrangement product (20; R^1 = R^2 = Ph), identical with an authentic sample prepared by the method of Lazaris, Shmuilovich, and Egorochkin.[9]

We have also prepared three further examples of meso-ionic aminotriazoliumthiolates (20; R^1 = Me, R^2 = Me or Ph; R^1 = Ph, R^2 = Me) using the procedure described by Lazaris *et al.*[9] Condensation of compound (20; R^1 = Me, R^2 = Ph) with *p*-chlorobenzaldehyde gave the triazoliumthiolate (18c) identical with the sample obtained by the rearrangement of compound (8c). In a similar manner, compound (18f) was also prepared.

The possibility that compound (20c) could rearrange in aqueous ethanolic ammonia solution has also been investigated. However, after 10 days, some starting material was recovered and attempts to separate the complex reaction mixture were unrewarding.

When a solution of the thiadiazoliumhydrazinide (9c; X = Cl) in ethanol was heated under reflux, the deep red colour of the solution rapidly turned to yellow. The product isolated was identified as the thiadiazolium chloride (23c).

It has been reported [9] that reaction of the triazoliumthiolate (20; R^1 = R^2 = Ph) with nitrous acid results in the formation of the triazole-thiol (31). We have re-investigated this reaction and obtained a single product which we have formulated as the disulphide (30; R^1 = R^2 = Ph). This structure is fully supported by its spectroscopic properties. Furthermore, we have prepared an authentic sample of this disulphide (30;



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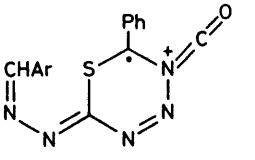

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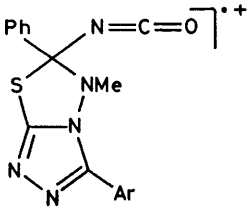

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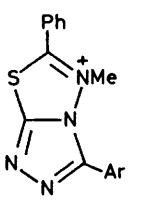

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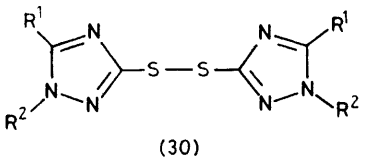
R^1 = R^2 = Ph) by oxidation of the thiol (31; R^1 = R^2 = Ph) using either iodine and sodium ethoxide or nitrous acid. In a similar manner reaction of the thiolates (20; R^1 = R^2 = Me; R^1 = Me, R^2 = Ph; or

R^1 = Ph, R^2 = Me) with nitrous acid gave the corresponding disulphides (31).

Treatment of the disulphide (31; $R^1 = R^2$ = Ph) with Raney nickel gave *N'*-cyano-*N*-phenylbenzamidine (32)



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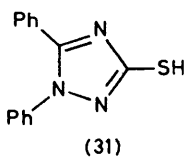

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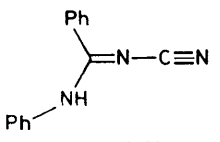

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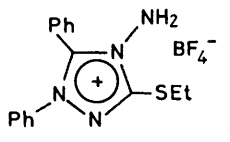

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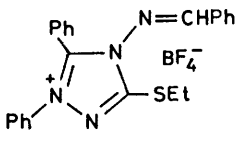

(34)

whose constitution was confirmed by its synthesis from *N*-phenylbenzimidoyl chloride and cyanamide.

The meso-ionic thiadiazolium- and triazolium-benzylidenehydrazinide rings (8) and (10) are associated with azomethine imine 1,3-dipoles and might therefore be expected to participate in 1,3-dipolar cycloaddition reactions.[2,10] The thiadiazoliumbenzylidenehydrazinide (8a) was unchanged when heated under reflux (4 days) with diphenylacetylene in benzene solution. When dimethylacetylene dicarboxylate, tetracyanoethylene, or dimethyl azodicarboxylate were investigated as possible 1,3-dipolarophiles, complex mixtures were formed from which no pure product could be isolated. However, addition of an acetone solution of compound (8c) to a solution of the triazoline dione (24) in acetone gave almost instantaneously an orange precipitate which was identified as the 1,3-dipolar cycloadduct (25c). In a similar manner, the adduct (25a) was also prepared.

In their i.r. spectra, the 1,3-dipolar cycloadducts (25) show characteristic C=O stretching vibrations (1 700 cm^{-1}) and C=N stretching (1 580—1 560 cm^{-1}). The structures of the adducts (25) are also supported by their mass spectral fragmentation pattern. The weak molecular ions give fragment ions whose constitutions have been determined by high resolution measurements and which can be represented by the structures (26)—(29).

Treatment of compound (20; $R^1 = R^2$ = Ph) with triethyloxonium tetrafluoroborate yielded the *S*-alkylated tetrafluoroborate salt (33). In a similar reaction, compound (18f) gave the corresponding *S*-alkylated salt (34). The reactions of the salts (33) and (34) with nucleophiles failed to give isolable products.

EXPERIMENTAL

General experimental details are given in Part 8.[10]

5-(Benzylidenehydrazino)tetrazoles (6).—A solution of sodium nitrite (7.2 g) in water (80 ml) was added to a solution of 5-aminotetrazole [7] (10.4 g) and sodium carbonate (5.6 g) in water (80 ml). This aqueous solution was then added dropwise with stirring to an ice-cold solution of concentrated hydrochloric acid (40 ml) in water (240 ml) and the temperature was maintained at 0—5°. *The total volume of the solution at the end of the diazotisation must exceed 400 ml to avoid explosions.* When the addition was complete, the solution was rapidly poured into a chilled solution of hydrated tin(II) chloride (60.0 g) in concentrated hydrochloric acid (80.0 ml). A small amount of solid was filtered off and 4-tolualdehyde (10 ml) added to the filtrate. On shaking, a solid separated and the reaction was completed by heating on a steam-bath (1 h). After cooling, the solid was collected and recrystallised from ethanol, giving *5-(4-methylbenzylidenehydrazino)tetrazole* (6b) (9.3 g, 38%) as needles, m.p. 240° (decomp.) (Found: C, 53.2; H, 5.2; N, 41.5%; $M^{\cdot+}$, 202. $C_9H_{10}N_6$ requires C, 53.5; H, 4.95; N, 41.6%; *M*, 202); $\nu_{max.}$ (KBr) 3 400, 3 000br, and 1 630 cm^{-1}; τ[$(CD_3)_2SO$] −1.1 (s, NH), 1.9 (s, CH), 2.3 and 2.75 (A_2B_2, J_{AB} 7 Hz, 4 ArH), and 7.7 (s, Me).

The following compounds were similarly prepared: 5-(benzylidenehydrazino)tetrazole (6a) (14.0 g, 50%), needles, m.p. 235—236° (decomp.) (lit.,[7] 235°); $\nu_{max.}$ (KBr) 3 000br and 1 630 cm^{-1}; 5-(4-chlorobenzylidenehydrazino)tetrazole (6c) (12.0 g, 46%), prisms, m.p. 231—233° (decomp.) (lit.,[7] 233°); $\nu_{max.}$ (KBr) 3 000br and 1 640 cm^{-1}; *5-(4-methoxybenzylidenehydrazino)tetrazole* (6d) (13.0 g, 48%), prisms, m.p. 235—237° (decomp.) (Found: C, 49.3; H, 4.8; N, 38.8%; $M^{\cdot+}$, 218. $C_9H_{10}N_6O$ requires C, 49.5; H, 4.6; N, 38.5%; *M*, 218); $\nu_{max.}$ (KBr) 3 300, 3 000br, and 1 650 cm^{-1}; τ[$(CD_3)_2SO$] −1.6 (s, NH), 1.9 (s, CH), 2.2 and 3.1 (A_2B_2, J_{AB} 8 Hz, 4 ArH), and 6.2 (s, OMe).

1,1-Dibromo-4-(4-substituted aryl)-2,3-diazabuta-1,3-dienes (4).—5-(4-Methylbenzylidenehydrazino)tetrazole (6b) (3.0 g) in glacial acetic acid (900 ml) and water (900 ml) was stirred at 0°. A solution of bromine in glacial acetic acid (30 ml; 15% w/v) was added dropwise, with the temperature maintained at 0—5°. After the addition was completed, the mixture was diluted to 3.5 l and extracted with methylene chloride. The organic layer was washed, dried, and evaporated. The residue was dissolved in hot n-hexane (50 ml) and filtered, and evaporation of the filtrate gave *1,1-dibromo-4-(4-tolyl)-2,3-diazabuta-1,3-diene* (4b) (1.4 g, 31%) as a pale yellow oil (Found: C, 35.65; H, 2.9; Br, 52.9; N, 9.0; $M^{\cdot+}$, 302. $C_9H_8BrN_2$ requires C, 35.5; H, 2.6; Br, 52.6; N, 9.2%; *M*, 302); $\nu_{max.}$ (film) 1 600 and 1 570 cm^{-1}; τ 1.59 (s, CH), 2.16 and 2.66 (A_2B_2, J_{AB} 6 Hz, 4 ArH), and 7.56 (s, Me).

The following compounds were similarly prepared: 1,1-dibromo-4-phenyl-2,3-diazabuta-1,3-diene (4a) (2.1 g, 45%), pale yellow oil (lit.,[5] 15—17°); $\nu_{max.}$ (film) 1 690, 1 610, and 1 570 cm^{-1}; 1,1-dibromo-4-(4-chlorophenyl)-2,3-diazabuta-1,3-diene (4c) (2.0 g, 46%), pale yellow needles, m.p. 93—94° (lit.,[5] 92—93°); $\nu_{max.}$ (KBr) 1 600 cm^{-1}; 1,1-dibromo-4-(4-methoxyphenyl)-2,3-diazabuta-1,3-diene (4d) (1.6, 37%), pale yellow plates, m.p. 60—62° (lit.,[5] 60—61°); $\nu_{max.}$ (KBr) 1 600 cm^{-1}.

2-Benzylidenehydrazino-4-methyl-5-phenyl-1,3,4-thiadiazolium Bromides (7).—A solution of 1,1-dibromo-4-phenyl-2,3-diazabuta-1,3-diene (0.30 g) and *N*-methyl-*N*-thiobenzoyl hydrazine [11] (0.17 g) in benzene (8 ml) was heated

under reflux (1.5 h). After cooling, the solid product was collected and recrystallised from ethanol–light petroleum (b.p. 60—80°) giving *2-benzylidenehydrazino-4-methyl-5-phenyl-1,3,4-thiadiazolium bromide* (7a) (0.17 g, 42%) as pale yellow prisms, m.p. 220—222° (Found: C, 51.5; H, 4.1; Br, 21.5; N, 15.2; S, 8.75. $C_{16}H_{15}BrN_4S$ requires C, 51.2; H, 4.0; Br, 21.3; N, 14.9; S, 8.5%); $\nu_{max.}$ (KBr) 2 600, 1 600, 1 580, and 1 420 cm^{-1}; τ 1.15 (s, CH), 1.9—2.8 (m, 10 ArH), and 5.69 (s, NMe), *m/e* 294 ($M^{\cdot+}$ — HBr).

The following compounds were similarly prepared: *4-methyl-2-(4-methylbenzylidenehydrazino)-5-phenyl-1,3,4-thiadiazolium bromide* (7b) (0.17 g, 45%), buff needles, m.p. 204—205° (Found: C, 52.5; H, 4.6; Br, 20.4; N, 14.6; S, 8.35. $C_{17}H_{17}BrN_4S$ requires C, 52.4; H, 4.4; Br, 20.6; N, 14.4; S, 8.2%); $\nu_{max.}$ (KBr) 2 800—2 600, 1 600, 1,580, and 1 430 cm^{-1}; τ 1.2 (s, CH), 1.9—2.9 (m, 9 ArH), 5.7 (s, NMe), and 7.6 (s, CMe); *m/e* 308 ($M^{\cdot+}$ — HBr); *2-(4-chlorobenzylidenehydrazino)-4-methyl-5-phenyl-1,3,4-thiadiazolium bromide* (7c) (0.27 g, 55%), brown-yellow prisms, m.p. 191—192° (Found: C, 46.9; H, 3.7; Br, 19.35; Cl, 8.6; N, 13.8; S, 8.0. $C_{16}H_{14}BrClN_4S$ requires C, 46.9; H, 3.4; Br, 19.3; Cl, 8.7; N, 13.7; S, 7.8%); $\nu_{max.}$ (KBr) 2 900, 2 650, 1 600, 1 500, and 1 440 cm^{-1}; τ 1.2 (s, CH), 2.0—2.8 (m, 9 ArH), and 5.7 (s, NMe); *m/e* 328 [$M^{\cdot+}$-(^{35}Cl) — HBr]; *2-(4-methoxybenzylidenehydrazino)-4-methyl-5-phenyl-1,3,4-thiadiazolium bromide* (7d) (0.24 g, 49%), green-yellow needles, m.p. 199—200° (Found: C, 50.4; H, 4.5; Br, 19.6; N, 13.5; S, 7.7. $C_{17}H_{17}BrN_4OS$ requires C, 50.4; H, 4.2; Br, 19.75; N, 13.8; S, 7.9%); $\nu_{max.}$ (KBr) 3 000—2 700br, 1 600, 1 500, 1 435, and 1 250 cm^{-1}; τ[$(CD_3)_2SO$] 1.7 (s, CH), 1.9—2.5 (m, 7 ArH), 2.95 (d, 2 ArH), 5.89 (s, NMe), and 6.19 (s, OMe); *m/e* 324 ($M^{\cdot+}$ — HBr); *2-(4-chlorobenzylidenehydrazino)-4.5-diphenyl-1,3,4-thiadiazolium bromide* (7e) (0.2 g, 51%), brown-yellow prisms, m.p. 255—256° [Found: ($M^{\cdot+}$ — HBr) 390.071 0. $C_{21}H_{16}BrClN_4S$ requires *M*, 390.070 6]; $\nu_{max.}$ (KBr) 3 400, 2 700, 1 600, 1 580, 1 490, and 1 440 cm^{-1}; τ(CD_3OD) 1.8 (s, CH), and 2.1—2.6 (m, 14 ArH).

4-Methyl-5-phenyl-1,3,4-thiadiazolium-2-benzylidenehydrazinides (8).—A suspension of the bromide (7a) (0.1 g) in methylene chloride (5 ml) was gently shaken while a stream of dry ammonia was passed over the solvent (2 min). The colour instantaneously changed from yellow to red. Ammonium bromide was filtered off and evaporation of the filtrate gave a residue which was recrystallised from benzene–n-hexane giving *4-methyl-5-phenyl-1,3,4-thiadiazolium-2-benzylidenehydrazinide* (8a) (0.06 g, 70%) as red-brown needles, m.p. 198—200° (Found: C, 65.2; H, 5.0; N, 18.9; S, 10.8%; $M^{\cdot+}$, 294. $C_{16}H_{14}N_4S$ requires C, 65.3; H, 4.8; N, 19.05; S, 10.9%; *M*, 294); $\lambda_{max.}$ 248, 333, and 434 nm (ε 19 640, 11 790, and 9 543); $\nu_{max.}$ (KBr) 1 590, 1 560, 1 460, and 1 430 cm^{-1}; τ 1.85 (s, CH), 2.1—2.8 (m, 10 ArH), and 6.1 (s, NMe).

The following compounds were similarly prepared: *4-methyl-5-phenyl-1,3,4-thiadiazolium-2-(4-methylbenzylidenehydrazinide)* (8b) (0.06 g, 76%), red prisms, m.p. 207—208° (Found: C, 66.35; H, 5.3; N, 18.1; S, 10.6%; $M^{\cdot+}$, 308. $C_{17}H_{16}N_4S$ requires C, 66.2; H, 5.2; N, 18.2; S, 10.4%; *M*, 308); $\lambda_{max.}$ 255, 335, and 438 nm (ε 28 800, 20 100, and 13 480); $\nu_{max.}$ (KBr) 1 600, 1 560, and 1 490—1 460 cm^{-1}; τ 1.8 (s, CH), 2.30—2.56 (m, 7 ArH), 2.87 (d, *J* 8 Hz, 2 ArH), and 6.10 (s, NMe); *4-methyl-5-phenyl-1,3,4-thiadiazolium-2-(4-chlorobenzylidenehydrazinide)* (8c) (0.06 g, 73%), orange-yellow prisms, m.p. 219—221° (Found: C, 58.5; H, 4.1; Cl, 10.5; N, 17.1; S, 9.7%; $M^{\cdot+}$, 328. $C_{16}H_{13}ClN_4S$ requires C, 58.4; H, 4.0; Cl, 10.8; N, 17.0; S, 9.7%; *M*, 328); $\lambda_{max.}$ 253, 342, and 438 nm (ε 23 800, 15 400, and 14 790); $\nu_{max.}$ (KBr) 1 600, 1 570, 1 490, and 1 470 cm^{-1}; τ 1.8 (s, CH), 2.2—2.8 (m, 9 ArH), and 6.1 (s, NMe); *4-methyl-5-phenyl-1,3,4-thiadiazolium-2-(4-methoxybenzylidenehydrazinide)* (8d) (0.08 g, 68%), dark red needles, m.p. 204—205° (Found: C, 63.2; H, 5.25; N, 17.4; S, 10.1%; $M^{\cdot+}$, 324. $C_{17}H_{16}N_4OS$ requires C, 63.0; H, 4.9; N, 17.3; S. 9.9%; *M*, 324); $\lambda_{max.}$ 253sh, 260, 335, and 440 nm (ε 16 686, 16 960, 16 524, and 13 650); $\nu_{max.}$ (KBr) 1 600, 1 560, 1 480—1 460, and 1 240 cm^{-1}; τ 1.94 (s, CH), 2.41 and 3.18 (A_2B_2, J_{AB} 8 Hz, 4 ArH), 1.48—1.58 (m, 5 ArH), 6.16 (s, NMe), and 6.22 (s, OMe); *4,5-diphenyl-1,3,4-thiadiazolium-2-(4-chlorobenzylidenehydrazinide)* (8e) (0.04 g, 47%), red prisms, m.p. 205—206° (Found: *M*, 390.070 6. $C_{21}H_{15}ClN_4S$ requires *M*, 390.070 6); $\lambda_{max.}$ 253, 346, and 454 nm (ε 25 700, 21 100, and 11 000); $\nu_{max.}$ (KBr) 1 600, 1 565, 1 510, 1 480, and 1 465 cm^{-1}; τ 1.9 (s, CH), and 2.3—2.7 (m, 14 ArH).

A solution of 1,1,4-trichloro-4-(4-chlorophenyl)-2,3-diazabuta-1,3-diene [6] (5c) (0.54 g) and *N*-methyl-*N*-thiobenzoylhydrazine [11] (0.33 g) in benzene (10 ml) was heated under reflux (3 h). After cooling and filtering, the sticky solid was washed with ether and dissolved in methylene chloride (10 ml). Triethylamine (0.5 ml) was added and the yellow solution immediately became deep red. The residue obtained by evaporation was dissolved in hot benzene (10 ml) and triethylamine hydrochloride was filtered off. Concentration of the benzene solution gave *4-methyl-5-phenyl-1,3,4-thiadiazolium-2-(α,4-dichlorobenzylidenehydrazinide)* (9c; X = Cl) (0.23 g, 32%) as red prisms, m.p. 168—169° [Found: C, 52.6; H, 3.6; Cl, 19.5; N, 15.4; S, 8.9%; $M^{\cdot+}$(^{35}Cl), 362. $C_{16}H_{12}Cl_2N_4S$ requires C, 52.9; H, 3.3; Cl, 19.6; N, 15.4; S, 8.8%; *M*(^{35}Cl), 362]; $\lambda_{max.}$ (CH_2Cl_2) 345 and 445 nm (ε 15 630 and 15 180); $\nu_{max.}$ (KBr) 1 580, 1 568, and 1 470 cm^{-1}; τ 2.20 and 2.78 (A_2B_2, J_{AB} 8 Hz, 4 ArH), 2.53 (s, 5 ArH), and 6.12 (s, NMe).

The foregoing compound (9c; X = Cl) (15 mg) in benzene (5.0 ml) was stirred (12 h) at room temperature with a solution of potassium cyanide (3 mg) in dimethylformamide (4.0 ml). The two layers were separated and the dimethylformamide solution washed with benzene (2 × 5 ml). Evaporation of the combined benzene solutions and recrystallisation of the residue from benzene gave *4-methyl-5-phenyl-1,3,4-thiadiazolium-2-(4-chloro-α-cyanobenzylidenehydrazinide)* (9c; X = CN) (11 mg, 75%) as red prisms, m.p. 246—248° (Found: $M^{\cdot+}$ 353.050 4. $C_{17}H_{12}N_5ClS$ requires *M*, 353.050 2); $\lambda_{max.}$ 259, 351, and 457 nm (ε 17 840, 7 845, and 17 840); $\nu_{max.}$ (KBr) 2 200, 1 540, 1 480, 1 420, and 1 380 cm^{-1}.

3-Benzylidenehydrazino-1-methyl-4,5-diphenyl-1,2,4-triazolium Bromides (11).—A solution of 1,1-dibromo-4-phenyl-2,3-diazabuta-1,3-diene (0.29 g) and *N*-amino-*N*-methyl-*N'*-phenylbenzamidine [12] (0.23 g) in chloroform (15 ml) was heated under reflux (2 h). Evaporation gave a solid residue which was dissolved in ethanol (8 ml) and added dropwise with stirring to ether (50 ml). The precipitated salt was recrystallised from ethanol–light petroleum (b.p. 60—80°) and identified as *3-benzylidenehydrazino-1-methyl-4,5-diphenyl-1,2,4-triazolium bromide* (11a) (0.17 g, 40%), buff platelets, m.p. 260—262° (Found: C, 60.5; H, 4.6; Br, 18.5; N, 16.1. $C_{22}H_{20}BrN_5$ requires C, 60.8; H, 4.6; Br, 18.4; N, 16.1%) $\nu_{max.}$ (KBr) 1 600, 1 480, and 1 370 cm^{-1}; τ[$(CD_3)_2SO$] 1.78 (s, CH), 2.2—2.7 (m, 15 ArH + NH), and 6.10 (s, NMe); *m/e* 353 ($M^{\cdot+}$ — HBr).

The following compounds were similarly prepared: 1-*methyl*-3-(4-*methylbenzylidenehydrazino*)-4,5-*diphenyl*-1,2,4-*triazolium bromide* (11b) (0.17 g, 40%), prisms, m.p. 247—248° (Found: C, 61.7; H, 5.2; Br, 17.7; N, 15.7. $C_{23}H_{22}BrN_5$ requires C, 61.6; H, 4.9; Br, 17.9; N, 15.6%); $\nu_{max.}$ (KBr) 3 400, 3 100—2 700, 1 600, and 1 570 cm^{-1}; τ 1.28 (s, CH), 2.0—3.0 (m, 14 ArH), 6.07 (s, NMe), and 7.73 (s, CMe); *m/e* 367 ($M^{\cdot+}$ — HBr); 3-(4-*chlorobenzylidenehydrazino*)-1-*methyl*-4,5-*diphenyl*-1,2,4-*triazolium bromide* (11c) (0.24 g, 51%), prisms, m.p. 210—212° (Found: C, 56.2; H, 4.3; Br, 16.8; Cl, 7.4; N, 15.2. $C_{22}H_{19}BrClN_5$ requires C, 56.35; H, 4.1; Br, 17.1; Cl, 7.6; N, 14.9%); $\nu_{max.}$ 3 400, 3 100—2 850, 1 625br, and 1 590 cm^{-1}; *m/e* 387 [$M^{\cdot+}(^{35}Cl)$ — HBr]; 3-(4-*methoxybenzylidenehydrazino*)-1-*methyl*-4,5-*diphenyl*-1,2,4-*triazolium bromide* (11d) (0.23 g, 49%), prisms, m.p. 246—248° (Found: C, 59.2; H, 5.0; N, 15.2. $C_{23}H_{22}BrN_5O$ requires C, 59.5; H, 4.7; N, 15.1%); $\nu_{max.}$ (KBr) 3 400, 3 000—2 800, 1 620br, 1 580, and 1 500 cm^{-1}; *m/e* 383 ($M^{\cdot+}$ — HBr).

1-*Methyl*-4,5-*diphenyl*-1,2,4-*triazolium*-3-*benzylidenehydrazidines* (10).—A suspension of 3-benzylidenehydrazino-1-methyl-4,5-diphenyl-1,2,4-triazolium bromide (11a) (0.1 g) in methylene chloride (8 ml) was gently shaken while dry ammonia was passed over the mixture (2 min). An immediate colour change from pale brown to deep yellow occurred. Ammonium bromide was filtered off and evaporation of the filtrate gave a solid residue which was recrystallised from benzene–n-hexane and identified as 1-*methyl*-4,5-*diphenyl*-1,2,4-*triazolium*-3-*benzylidenehydrazinide* (10a) (0.06 g, 75%), bright yellow prisms, m.p. 231—233° (Found: C, 74.8; H, 5.6; N, 20.1%; $M^{\cdot+}$, 353.163 7. $C_{22}H_{19}N_5$ requires C, 74.8; H, 5.4; N, 19.8%; *M*, 353.164 0); $\lambda_{max.}$ 303 and 357 nm (ε 9 456 and 7 941); $\nu_{max.}$ (KBr) 1 600, 1 550, 1 520, 1 480, 1 440, and 1 415 cm^{-1}; τ 1.85 (s, CH), 2.24—2.94 (m, 15 ArH), and 6.16 (s, NMe).

The following compounds were similarly prepared: 1-*methyl*-4,5-*diphenyl*-1,2,4-*triazolium*-3-(4-*methylbenzylidenehydrazinide*) 10b) (0.07 g, 63%), bright yellow prisms, m.p. 246—247° (Found: $M^{\cdot+}$, 367.179 7. $C_{23}H_{21}N_5$ requires *M*, 367.179 7); $\lambda_{max.}$ 308 and 357 nm (ε 14 530 and 20 800); $\nu_{max.}$ (KBr) 1 595, 1 560, 1 530, 1 485, and 1 430 cm^{-1}; τ 1.80 (s, CH), 2.25—3.0 (m, 14 ArH), 6.18 (s, NMe), and 7.68 (s, CMe); 1-*methyl*-4,5-*diphenyl*-1,2,4-*triazolium*-3-(4-*chlorobenzylidenehydrazinide*) (10c) (0.09 g, 74%), bright yellow prisms, m.p. 253—255° [Found: C, 68.1; H, 4.5; Cl, 9.2; N, 17.8%; $M^{\cdot+}(^{35}Cl)$, 387. $C_{22}H_{18}ClN_5$ requires C, 68.1; H, 4.65; Cl, 9.2; N, 18.1%; *M*, 387]; $\lambda_{max.}$ 310 and 367 nm (ε 22 250 and 33 170); $\nu_{max.}$ (KBr) 1 600, 1 560, 1 520, 1 480, and 1 450—1 420 cm^{-1}; τ 1.90 (s, CH), 2.3—3.0 (m, 14 ArH), and 6.16 (s, NMe); 1-*methyl*-4,5-*diphenyl*-1,2,4-*triazolium*-3-(4-*methoxybenzylidenehydrazinide* (10d) (0.07 g, 66%), golden-yellow prisms, m.p. 224—226° (Found: C, 71.8; H, 5.6; N, 18.0%; $M^{\cdot+}$, 383. $C_{23}H_{21}N_5O$ requires C, 72.1; H, 5.5; N, 18.3%; *M*, 383); $\lambda_{max.}$ 306sh, 330sh, and 353 nm (ε 24 840, 29 010, and 32 670); $\nu_{max.}$ (KBr) 1 600, 1 570sh, 1 550, and 1 495 cm^{-1}; τ 1.88 (s, CH), 2.2—2.8 (m, 12 ArH), 3.16 (d, *J* 4.5 Hz, 2 ArH), 6.17 (s, 3 H), and 6.20 (s, 3 H).

Reaction of N-*Benzoyl*-N-*methylhydrazine with* 1,1-*Dibromo*-4-(4-*chlorophenyl*)-2,3-*diazabuta*-1,3-*diene*.—A solution of *N*-benzoyl-*N*-methylhydrazine [13] (0.75 g) and 1,1-dibromo-4-(4-chlorophenyl)-2,3-diazabuta-1,3-diene (1.6 g) in methylene chloride (25 ml) was heated under reflux (3 h) and the colourless solution was then evaporated to half its original volume, keeping the temperature below 30°. Addition of n-pentane (15 ml) to the residue gave a colourless solid which was collected, and further concentration and trituration with n-pentane gave a second batch. Recrystallisation from ethanol gave N-*benzoyl*-N′-4-*chlorobenzylidene*-N-*methylhydrazine* (14c) (0.97 g) as plates, m.p. 152—153° (Found: C, 66.0; H, 4.9; N, 10.4% $M^{\cdot+}$, 272. $C_{15}H_{13}ClN_2O$ requires C, 66.0; H, 4.8; N, 10.1%; *M*, 272); $\nu_{max.}$ (KBr) 1 650, 1 600, 1 460, 1 400, 1 330, 1 050, and 1 025 cm^{-1}; τ 2.1—2.7 (m, 9 ArH + 1 CH–) and 6.45 (s, NMe). Evaporation of the pentane liquors at room temperature gave a colourless oil which decomposed either on warming or on t.l.c. plates. This oil was identified as dibromo(hydrazono)methane ($H_2N{\cdot}N{=}CBr_2$); $\nu_{max.}$ (film) 3 300 and 1 600 cm^{-1}; *m/e* 200 [$M^{\cdot+}(^{79}Br)$] and 121 [$M^{\cdot+}(^{79}Br)$ — ^{79}Br], and this structure was confirmed by reaction with *p*-chlorobenzaldehyde and anisaldehyde (*vide infra*).

Reaction of Dibromo(hydrazono)methane with Aromatic Aldehydes.—Dibromo(hydrazono)methane (0.2 g) in ether (5 ml) was added to a solution of *p*-chlorobenzaldehyde (0.14 g) in ether (3 ml) and the mixture set aside at room temperature (12 h). Evaporation gave a solid which was recrystallised from n-hexane and identified as the diazabutadiene (4c) (0.23 g, 68%), pale yellow needles, m.p. 93—94°, identical with an authentic sample.

In the same way, compound (4d) (0.15 g, 45%), plates, m.p. 63—64°, was prepared and found to be identical with an authentic sample.

Reaction of 4-*Methyl*-5-*phenyl*-1,3,4-*thiadiazolium*-2-(4-*chlorobenzylidenehydrazinide*) (8c) *with Aqueous Ethanolic Ammonia*.—Concentrated ammonia solution (s.g., 0.88) (5 ml) was added to a solution of compound (8c) (0.15 g) in ethanol (20 ml) and the mixture heated under reflux (10 days). At regular intervals (24 h) the solution was saturated with ammonia gas. The red colour of the solution slowly changed to pale yellow. Evaporation gave a solid residue which was purified by t.l.c. (silica gel: chloroform–ethanol, 9 : 1). The faster-running component was extracted with chloroform, recrystallised from benzene–n-hexane, and identified as 4-(N-4-*chlorobenzylideneamino*)-1-*methyl*-5-*phenyl*-1,2,4-*triazolium*-3-*thiolate* (18c) (8 mg), pale yellow prisms, m.p. 215—216° (Found: C, 58.2; H, 4.2; N, 16.9%; $M^{\cdot+}$, 328.054 1. $C_{16}H_{13}ClN_4S$ requires C, 58.4; H, 4.0; N, 17.0%; *M*, 328.054 9); $\lambda_{max.}$ 248, 277sh, 283, and 300sh nm (ε 6 315, 5 169, 5 262, and 3 552); $\nu_{max.}$ (KBr) 1 600, 1 580, 1 500, 1 460, 1 360, and 1 290 cm^{-1}.

The slower-running component was extracted with ethanol. Recrystallisation from ethanol gave 4-*amino*-1-*methyl*-5-*phenyl*-1,2,4-*triazolium*-3-*thiolate* (20) (92 mg) as colourless needles, m.p. 183—185° (decomp.) (Found: C, 52.3; H, 5.1; N, 26.7%; $M^{\cdot+}$, 206.062 4. $C_9H_{10}N_4S$ requires C, 52.4; H, 4.85; N, 26.7%; *M*, 206.062 6); $\lambda_{max.}$ 245 and 309 nm (ε 15 770 and 2 446); $\nu_{max.}$ (KBr) 3 350, 3 250, 1 520, 1 480, 1 440, 1 380, 1 340, 1 235, and 1 190 cm^{-1}; τ[$(CD_3)_2SO$] 2.17—2.50 (m, 5 ArH), 4.19 (s, NNH_2; disappears on shaking the solution with D_2O), and 6.29 (s, NMe).

4-Amino-1,5-diphenyl-1,2,4-triazolium-3-thiolate (20; $R^1 = R^2 = Ph$) was similarly prepared (0.054 g, 38%), needles, m.p. 218—219° (lit.,[9] 215—216°) (Found: C, 62.5; H, 4.7; N, 20.9; S, 12.2%; $M^{\cdot+}$, 268. Calc. for $C_{14}H_{12}N_4S$: C, 62.7; H, 4.5; N, 20.9; S, 11.9%; *M*, 268); $\lambda_{max.}$ 248 and 323 nm (ε 23 130 and 3 190); $\nu_{max.}$ (KBr) 3 280, 3 220, 3 200, 1 624, 1 598, 1 510, 1 384, and 1 356

cm^{-1}; τ[$(CD_3)_2SO$] 2.3—2.8 (m, 10 ArH), and 3.9 (s, $N-NH_2$; removed by D_2O).

4-Amino-1,2,4-triazolium-3-thiolates (20).—Carbon disulphide (8.0 ml) was added with stirring to a cooled mixture of *N*-benzoyl-*N*-phenylhydrazine hydrochloride (20.0 g) and triethylamine (50 ml), and the mixture set aside at room temperature (1 h). A solution of sodium chloroacetate (10.0 g) in water (150 ml) was added and the mixture heated until dissolution was complete. The solution was treated with hydrazine hydrate (8.0 ml) and heated under reflux (1 h). After cooling, the solid was collected and recrystallised from dimethylformamide–ethanol giving 4-amino-1,5-diphenyl-1,2,4-triazolium-3-thiolate (20; $R^1 = R^2 = Ph$) (9.05 g, 42%) as needles, m.p. 218—219° (lit.,[9] 215—216°), identical with an authentic sample (see before).

The following compounds were similarly prepared: 4-amino-1-methyl-5-phenyl-1,2,4-triazolium-3-thiolate (20; $R^1 = Me$, $R^2 = Ph$) (8.6 g, 39%) as plates, m.p. 191—192°, identical with an authentic sample (see before); *4-amino-5-methyl-1-phenyl-1,2,4-triazolium-3-thiolate* (20; $R^1 = Ph$, $R^2 = Me$) (10.0 g, 45%), as plates, m.p. 216—218° (decomp.) (Found: C, 52.5; H, 5.1; N, 27.3; S, 15.3%; $M^{\cdot+}$, 206. $C_9H_{10}N_4S$ requires C, 52.4; H, 4.9; N, 27.2; S, 15.5%; *M*, 206); $\lambda_{max.}$ 243 and 288 nm (ε 18 140 and 5 908); $\nu_{max.}$ (KBr) 3 240, 3 100, 1 632, 1 600, 1 565, 1 531, 1 490, 1 420, 1 380, 1 370, and 1 360 cm^{-1}; τ[$(CD_3)_2SO$] 2.3—2.5 (m, 5 ArH), 4.04 (s, NH_2, removed by D_2O), and 7.40 (s, Me); *4-amino-1,5-dimethyl-1,2,4-triazolium-3-thiolate* (20; $R^1 = R^2 = Me$) (6.6 g, 29%), prisms, m.p. 228—229° (decomp.) (Found: C, 33.6; H, 5.6; N, 39.0; S, 21.9%; $M^{\cdot+}$, 144. $C_4H_8N_4S$ requires C, 33.3; H, 5.6; N, 38.9; S, 22.2%; *M*, 144); $\lambda_{max.}$ 241 nm (ε 13 020); $\nu_{max.}$ (KBr) 3 240, 3 120, 1 640, 1 600, 1 530, 1 380, 1 360, and 1 230 cm^{-1}; τ[$(CD_3)_2SO$] 4.30 (s, NNH_2, removed by D_2O), 6.30 (s, NMe), and 7.50 (s, Me).

4-(N-4-Chlorobenzylideneamino)-1-methyl-5-phenyl-1,2,4-triazolium-3-thiolate (18c).—A suspension of the foregoing triazoliumthiolate (20; $R^1 = Me$, $R^2 = Ph$) (1.0 g) and anhydrous sodium acetate (0.25 g) in glacial acetic acid (10 ml) containing *p*-chlorobenzaldehyde (0.75 g) was heated under reflux (20 min). Addition of water (40 ml) caused precipitation of a yellow solid, which was recrystallised from benzene–light petroleum (b.p. 60—80°) giving the triazoliumthiolate (18c) (0.6 g, 38%) as yellow prisms, m.p. 209—210°, identical with the sample already described.

4-(*N*-Benzylideneamino)-1,5-diphenyl-1,2,4-triazolium-3-thiolate (18f) was prepared similarly (1.1 g, 81%), yellow needles, m.p. 226—227° (lit.,[9] 224°) (Found: C, 70.5; H, 4.8; N, 15.85; S, 9.1%; $M^{\cdot+}$, 356. Calc. for $C_{21}H_{16}N_4S$: C, 70.8; H, 4.55; N, 15.7; S, 9.0%; *M*, 356); $\lambda_{max.}$ 250 and 352 nm (ε 10 790 and 9 490); $\nu_{max.}$ (KBr) 3 060, 1 680, 1 600, 1 510, 1 480, 1 450, 1 370, and 1 160 cm^{-1}; τ(CF_3CO_2H) 1.2 (s, CH) and 2.0—2.7 (m, 15 ArH).

Reaction of 4-Amino-1,5-diphenyl-1,2,4-triazolium-3-thiolate (20; $R^1 = R^2 = Ph$) *with Nitrous Acid.*—Sodium nitrite (0.25 g) was added in small portions to a stirred solution of 4-amino-1,5-diphenyl-1,2,4-triazolium-2-thiolate (20; $R^1 = R^2 = Ph$) (0.9 g) in concentrated hydrochloric acid (10.0 ml) at 0°. The stirring was continued (1 h) and the reaction mixture diluted with water (30 ml). The precipitated solid was filtered off and recrystallised from dimethylformamide–ethanol giving bis-(1,5-diphenyl-1,2,4-triazol-3-yl) disulphide (30; $R^1 = R^2 = Ph$) (0.40 g, 47.5%) as needles, m.p. 178° (lit.,[14] 182—183°) (Found: C, 66.9; H, 4.2; N, 16.9; S, 12.8%; $M^{\cdot+}$, 504. Calc. for $C_{28}H_{20}N_6S_2$: C, 66.6; H, 4.0; N, 16.7; S, 12.7%; *M*, 504); $\lambda_{max.}$ 223 and 257 nm (ε 18 140 and 3 150); $\nu_{max.}$ (KBr) 3 060, 1 595, 1 500, 1 470, 1 450, 1 425, 1 300, 1 280, and 1 265 cm^{-1}; τ[$(CD_3)_2SO$] 2.4—2.8 (m, ArH).

The following compounds were similarly prepared: *bis-(1-methyl-5-phenyl-1,2,4-triazol-3-yl) disulphide* (30; $R^1 =$ Ph, $R^2 =$ Me) (2.1 g, 57%) as prisms, m.p. 112—113° (Found: C, 56.65; H, 4.35; N, 22.4; S, 17.0%; $M^{\cdot+}$, 380. $C_{18}H_{16}N_6S_2$ requires C, 56.8; H, 4.3; N, 22.1; S, 16.85%; *M*, 380); $\lambda_{max.}$ 223 nm (ε 24 970); $\nu_{max.}$ (KBr) 1 470, 1 460, 1 420, 1 400, 1 300, and 1 250 cm^{-1}; τ[$(CD_3)_2SO$] 2.18—2.72 (m, 10 ArH) and 6.1 (s, 6 H, Me); *bis-(5-methyl-1-phenyl-1,2,4-triazole-3-yl) disulphide* (30; $R^1 =$ Me, $R^2 =$ Ph) (1.3 g, 35%) as prisms, m.p. 82—83° (Found: C, 56.8; H, 4.5; N, 22.3; S, 16.9%; $M^{\cdot+}$, 380. $C_{18}H_{16}N_6S_2$ requires C, 56.85; H, 4.2; N, 22.1; S, 16.9%; *M*, 380); $\lambda_{max.}$ 240 nm (ε 20 060); $\nu_{max.}$ (KBr) 1 590, 1 510, 1 440, 1 410, 1 360, 1 300, and 1 290 cm^{-1}; τ 2.55 (s, 10 ArH) and 7.5 (s, 6 H, Me); *bis-(1,5-dimethyl-1,2,4-triazole-3-yl) disulphide* (30; $R^1 = R^2 =$ Me) (0.50 g, 27%) as prisms, m.p. 174—176° (Found: *M*, 256.056 8. $C_8H_{12}N_6S_2$ requires *M*, 256.056 3); $\nu_{max.}$ (KBr) 1 585, 1 510, 1 430, and 1 375 cm^{-1}; τ(CD_3OD) 6.0 (s, 6 H, NMe) and 7.25 (s, 6 H, Me).

1,5-Diphenyl-1,2,4-triazole-3-thiol (31).—1-Benzoyl-1-phenylthiosemicarbazide (2.0 g)[15] was dissolved in a hot aqueous solution of sodium hydroxide (10 ml, 15% w/v) and the solution cooled and acidified. The precipitated solid was filtered off and recrystallised from ethanol giving 1,5-diphenyl-1,2,4-triazole-3-thiol (31) (0.63 g, 34%) as pale yellow needles, m.p. 188—188.5° (lit.,[15] 188°).

Bis-(1,5-diphenyl-1,2,4-triazol-3-yl) Disulphide (30; $R^1 = R^2 =$ Ph).—The foregoing thiol (31) (2.5 g) was dissolved in a solution of sodium ethoxide (0.7 g) in ethanol (30 ml) and iodine (1.0 g) was added. The solvent was evaporated off and the residue washed with water. The solid was recrystallised from dimethylformamide–ethanol giving the disulphide (30; $R^1 = R^2 =$ Ph) (1.6 g, 65%) as colourless prisms, m.p. 175°, identical with the sample already described.

Reaction of 1,5-Diphenyl-1,2,4-triazole-3-thiol (30; $R^1 = R^2 =$ Ph) *with Nitrous Acid.*—Sodium nitrite (0.6 g) was added in small portions to a stirred suspension of compound (30; $R^1 = R^2 =$ Ph) (2.0 g) in concentrated hydrochloric acid (20 ml) at 0°. The stirring was continued (1 h) and the mixture diluted with water (60 ml). The precipitated solid was filtered off and recrystallised from dimethylformamide–ethanol giving the disulphide (30; $R^1 = R^2 =$ Ph) (1.95 g, 98%) as needles, m.p. 177—178°, identical with an authentic sample.

Reaction of the Disulphide (30; $R^1 = R^2 =$ Ph) *with Raney Nickel.*—A suspension of compound (30; $R^1 = R^2 =$ Ph) (2.0 g) and Raney nickel (3.0 g) in ethanol (30 ml) was heated under reflux (3 h). The nickel was collected and washed with hot ethanol. Evaporation of the filtrate gave a solid which was recrystallised from ethanol giving *N'-cyano-N-phenylbenzamidine* (32) (0.75 g, 43%) as plates, m.p. 233—235° (Found: C, 76.1; H, 5.3; N, 19.25%; $M^{\cdot+}$, 221. $C_{14}H_{11}N_3$ requires C, 76.0; H, 5.0; N, 19.0%; *M*, 221); $\lambda_{max.}$ 231, 245, and 289 nm (ε 4 340, 2 960, and 12 330); $\nu_{max.}$ (KBr) 3 030, 2 180, 1 605, 1 590, 1 540, 1 500, 1 470, 1 450, 1 370, 1 300, and 1 240 cm^{-1}; τ[$(CD_3)_2SO$] −0.8 (s, NH, removed by D_2O) and 2.2—2.9 (m, 10 ArH),

identical with an authentic sample prepared by the following method.

Cyanamide (3.0 g) was added to a solution of *N*-phenylbenzimidoyl chloride (10.0 g) in dry benzene (20 ml) and the mixture heated under reflux (45 min). Evaporation yielded a white solid, which was recrystallised from ethanol giving *N'*-cyano-*N*-phenylbenzamidine (10.36 g, 73%) as colourless plates, m.p. 233°.

Reaction of Compound (8c) *with* 4-*Phenyl*-1,2,4-*triazoline*-3,5-*dione* (24).—Compound (8c) (18 mg) in dry acetone (2 ml) was added to a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (24) [16] (9 mg) in dry acetone (2 ml). Almost immediately an orange solid precipitated. The mixture was left at 0° for 1 h, and the precipitate collected and identified as 9-(4-*chlorobenzylidenehydrazono*)-10-*methyl*-4,7-*diphenyl*-8-*thia*-1,2,4,6,10-*penta-azatricyclo*[5.2.1.$0^{2,6}$]*decane*-3,5-*dione* (25c) (20 mg, 73%), orange solid, m.p. 219—221° (Found: C, 57.2; H, 3.9; Cl, 7.2; N, 19.2; S, 6.55. $C_{24}H_{18}N_7ClO_2S$ requires C, 57.2; H, 3.6; Cl, 7.05; N, 19.5; S, 6.35%); $\lambda_{max.}$ ($HCONMe_2$) 279, 349, and 451 nm (ε 14 270, 14 890, and 19 400); $\nu_{max.}$ (KBr) 1 700, 1 580, 1 550, 1 490, and 1 420 cm^{-1}.

9-*Benzylidenehydrazono*-10-*methyl*-4,7-*diphenyl*-8-*thia*-1,2,4,6,10-*penta-azatricyclo*[5.2.1.$0^{2,6}$]*decane*-3,5-*dione* (25a) was prepared similarly (19 mg, 79%), orange solid, m.p. 202—203° (Found: C, 61.1; H, 4.3; N, 20.7%; $M^{\cdot+}$, 469. $C_{24}H_{19}N_7O_2S$ requires C, 61.4; H, 4.05; N, 20.9%; *M*, 469); $\lambda_{max.}$ (DMF) 275, 346, and 451 nm (ε 12 760, 13 190, and 16 860); $\nu_{max.}$ ($HCONMe_2$) 1 700, 1 580sh, 1 560, 1 500, and 1 420 cm^{-1}.

Hydrolysis of 4-*Methyl*-5-*phenyl*-1,3,4-*thiadiazolium*-2-(α,-4-*dichlorobenzylidenehydrazinide*) (9c; X = Cl).—Compound (9c; X = Cl) (30 mg) in ethanol (5 ml) was heated under reflux (5 min). The colour changed from deep red to bright yellow. After cooling to room temperature, the ethanolic solution was added dropwise to ether (20 ml). The resulting precipitate was recrystallised from ethanol–light petroleum (b.p. 60—80°) and identified as 2-(4-*chlorobenzoylhydrazino*)-4-*methyl*-5-*phenyl*-1,3,4-*thiadiazolium chloride* (23c) (23 mg, 73%), yellow prisms, m.p. 169—171° (Found: C, 50.1; H, 4.0; Cl, 18.75; N, 14.6; S, 8.6. $C_{16}H_{14}Cl_2N_4OS$ requires C, 50.4; H, 3.7; Cl, 18.6; N, 14.7; S, 8.4%); $\nu_{max.}$ 3 400br and 1 590br cm^{-1}.

4-*Amino*-1,5-*diphenyl*-3-*ethylthio*-1,2,4-*triazolium Tetrafluoroborate* (33).—A mixture of the thiolate (20; R^1 = R^2 = Ph) (2.5 g) and a solution of triethyloxonium tetrafluoroborate (3.0 g) in dry dichloromethane (20 ml) was set aside at room temperature (24 h). The addition of anhydrous ether, with cooling, afforded a colourless crystalline solid, which was recrystallised from dichloromethane–ether giving 4-*amino*-1,5-*diphenyl*-3-*ethylthio*-1,2,4-*triazolium tetrafluoroborate* (33) (2.24 g, 62%) as colourless needles, m.p. 110—111.5° (Found: C, 50.25; H, 4.5; N, 14.7; S, 8.2. $C_{16}H_{17}N_4SBF_4$ requires C, 50.0; H, 4.5; N, 14.6; S, 8.35%); $\lambda_{max.}$ 229 and 270 nm (ε 17 850 and 6 970); $\nu_{max.}$ (KBr) 3 250, 1 620, 1 600, 1 540, 1 500, 1 480, 1 450, and 1 140—1 000br cm^{-1}; τ 2.2—2.7 (m, 10 ArH), 4.5 (s, NH_2, disappears with D_2O), 6.5—6.9 (q, CH_2), and 8.2—8.6 (t, Me); *m/e* 297 ($M^{\cdot+}$ − BF_4).

By a similar method 4-*benzylideneamino*-1,5-*diphenyl*-3-*ethylthio*-1,2,4-*triazolium tetrafluoroborate* (34) was prepared (1.9 g, 71%), needles, m.p. 170—171° (Found: C, 58.8; H, 4.7; N, 12.0; S, 7.1. $C_{23}H_{21}N_4SBF_4$ requires C, 58.5; H, 4.5; N, 11.9; S, 6.8%); $\lambda_{max.}$ 273 nm (ε 4 795); $\nu_{max.}$ (KBr) 3 060, 2 960, 1 600, 1 575, 1 520, 1 480, 1 450, and 1 120—980br cm^{-1}; τ[$(CD_3)_2CO$] 0.8 (s, CH), 1.9—2.6 (m, 15 ArH), 6.25—6.7 (q, CH_2), and 8.2—8.6 (t, Me); *m/e* 385 ($M^{\cdot+}$ − BF_4).

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