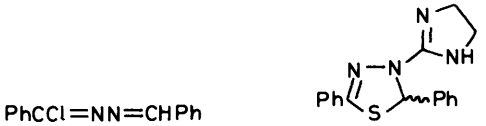
Thiadiazoles and Thiadiazolines. Part 2.[1] Δ^2-1,3,4-Thiadiazoline-4-carboxamidines Derived from Substituted Acyclic Thioureas

By **Stephen F. Moss** and **David R. Taylor,*** Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

A series of Δ^2-1,3,4-thiadiazoline-4-carboxamidines (2b—f) and the corresponding amidinium chlorides have been prepared in 70—92% yield by reactions between 1-chloro-1,4-diphenyl-2,3-diazabutadiene (1) and the following thioureas: *N*-methylthiourea, *N,N'*-dimethylthiourea, *N,N,N'*-trimethylthiourea, *N*-allylthiourea, and *N*-phenylthiourea. Their spectroscopic properties are discussed, with particular reference to the amidine tautomerism. Attempts to achieve corresponding reactions between compound (1) and sterically hindered thioureas were unsuccessful. *N,N'*-Diphenylthiourea was converted into 3-anilino-4,5-diphenyl-4*H*-1,2,4-triazole (6), initially isolated as its hydrochloride; *N,N'*-di-t-butylthiourea gave 2,5-diphenyl-1,3,4-thiadiazole (8) (36%), the 4-(1-diazabutadienyl)-Δ^2-1,3,4-thiadiazoline (9) (5%), di-t-butylurea (15%), and t-butylammonium chloride (6%). Mechanisms for these reactions are proposed.

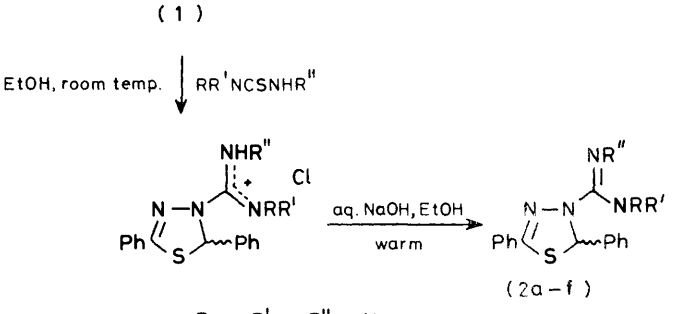
FOLLOWING our observation that 1-chloro-1,4-diphenyl-2,3-diazabutadiene (1) reacts with thiourea and ethylenethiourea to yield the hydrochlorides of 2,5-diphenyl-Δ^2-1,3,4-thiadiazoline-4-carboxamidines (2a) and (3),[1] we have investigated the scope of this new route to thiadiazolines using a selection of acyclic *N*-substituted thioureas. The reaction appears to be generally applic-



able, with the exception that *N,N'*-di-t-butyl- and *N,N'*-diphenyl-thiourea give cyclic products which arise by different pathways, indicating a steric limitation to the ring closure essential for thiadiazoline formation.

Reactions of 1-*Chloro*-1,4-*diphenyl*-2,3-*diazabutadiene* (1).—(a) *With* N-*methylthioureas*. *N*-Methyl-, *N,N'*-dimethyl-, and *N,N,N'*-trimethylthiourea were treated with the chlorodiazabutadiene at room temperature, and the resulting hydrochlorides (83—92%) were converted into the corresponding Δ^2-1,3,4-thiadiazoline-4-carboxamidines (2b—d) (Scheme 1) using aqueous hydroxide. The thiadiazolines were easily identified by n.m.r. spectroscopy, since they display the very characteristic proton (δ 7.0—7.2) and ^{13}C (δ 70.5—72.5 p.p.m.) resonances previously noted in the spectra of compound (2a).[1] Furthermore, we have now confirmed that in the corresponding hydrochlorides, which are more soluble in n.m.r. solvents than the hydrochloride of (2a) for which no satisfactory spectrum could be obtained, protonation occurs on the amidine unit and leaves the thiadiazoline ring unaffected (δ_H 7—8 and δ_C *ca.* 72 p.p.m.).

Relatively rapid tautomerism occurs in the amidine unit of the free bases (2b,c), leading to averaging of the two differently sited NH protons in (2b) and of the proton and ^{13}C signals of the two different *N*-methyl groups in (2c). None of the n.m.r. spectra gave any indication of geometrical isomerism due to restricted rotation about the C–N bonds in the amidine grouping. To verify that tautomerism was the cause of the equivalence of *N*-methyl signals, the ^1H n.m.r. spectrum of (2c) was re-run in $CDCl_3$ with the addition of varying amounts of the lanthanide shift reagent Eu(fod)$_3$. No resolution of different methyl signals was achieved. The ^1H n.m.r. spectrum of a solution of the hydrochloride of (2c) in trifluoroacetic acid did, however, display two lines in the *N*-methyl region; this was later shown to be



a; R = R' = R" = H
b; R = Me, R' = R" = H
c; R = R" = Me, R = H
d; R = R' = R" = Me
e; R = allyl, R' = R" = H
f; R" = Ph, R = R' = H

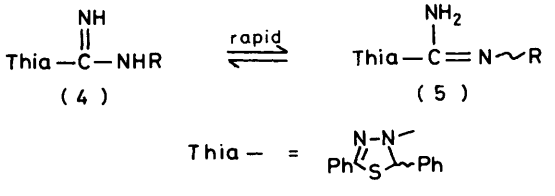
SCHEME 1

due to $\overset{+}{N}H$–CH coupling by means of a double-resonance experiment. The $CDCl_3$-soluble hydrochloride of (2d) displays three lines in the *N*-methyl region, interpreted as a 6H singlet (δ 3.1) and a 3H doublet (δ 2.7 $J_d \sim 5$ Hz) due to $\overset{+}{N}H$–CH coupling. This was confirmed not only by double-resonance irradiation at δ 10.3 but also by addition of D_2O, both experiments leading to collapse of the δ 2.7 doublet. These observations demonstrate that protonation of the thiadiazoline-4-carboxamidines (2) occurs in the 4-amidine unit and not at either of the ring nitrogen atoms.

(b) *With* N-*allylthiourea and* N-*phenylthiourea*. Treatment of the chlorodiazabutadiene (1) with *N*-allylthiourea yielded a hydrochloride (81%) which on brief treat-

ment with hot methanolic alkali gave an oil (100%) believed to be N^1-allylthiadiazoline-4-carboxamidine (2e) on the basis of its spectroscopic data. Attempted purification of the oil by molecular distillation led to thermal breakdown with the formation of benzonitrile, a fragmentation also observed in the mass spectra of these thiadiazolines (see below).

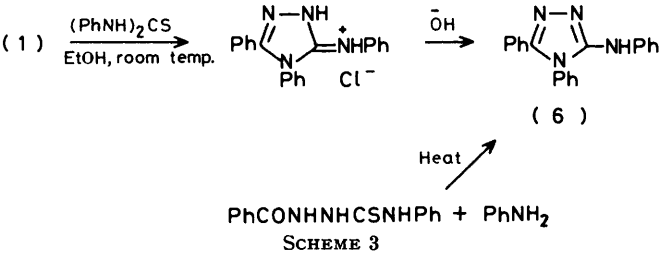
Although the tautomerism (Scheme 2) in the amidine



SCHEME 2

unit of this and the related *N*-methylamidine (2b) is rapid on the n.m.r. time-scale, a well-known phenomenon for *N*-alkylamidines,[2] the i.r. spectra of (2b) and (2e) indicate that the equilibrium favours the imino-form (4). Isomerism of this type has been thoroughly studied by i.r. spectroscopy:[3] the favoured isomer (4) is distinguished by =NH stretching (3 350—3 352 cm^{-1}) and RN–H stretching (3 455—3 452 cm^{-1}) modes. The analogous N^1-phenylthiadiazolinecarboxamidine (2f), obtained by a similar sequence from (1) and *N*-phenylthiourea, in contrast displays no =NH stretch but shows the characteristic asymmetric and symmetric stretching bands of a NH_2 group (3 512 and 3 405 cm^{-1}); evidently the *N*-phenyl group stabilises the =NPh form (5).

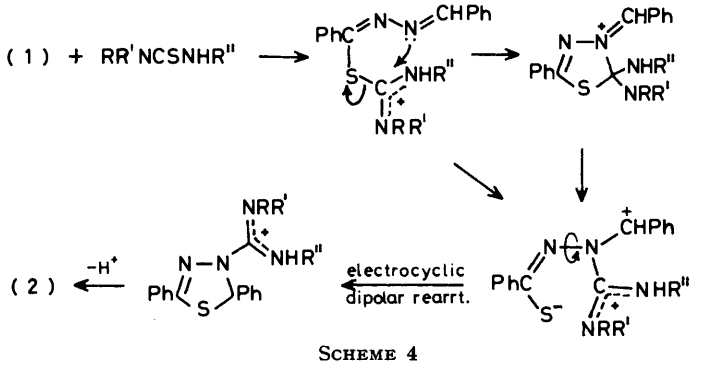
readily be explained by a changeover to nucleophilic attack on the imidoyl chloride (1) by NPh, since *N*-phenylthiourea reacts normally. More plausible is an



SCHEME 3

initial nucleophilic attack by the sulphur atom of *N*,*N*′-diphenylthiourea, and after ring closure is prevented by the size and charge delocalisation of the two *N*-phenyl groups the reaction is forced to proceed as in Scheme 5. Though detailed proof is lacking, we demonstrated that the aromatic group displaced is the one remote from the halogen atom in (1) by treating the 4-bromosubstituted analogue (7) with *N*,*N*′-diphenylthiourea. The hydrochloride (90%) obtained did not contain a bromophenyl group (Scheme 5).

(d) *With* N,N′-*di-t-butylthiourea*. It therefore seemed pertinent to investigate a reaction between the chlorodiazabutadiene and another sterically hindered thiourea. Di-t-butylthiourea, treated with compound (1) at ambient temperature, was rapidly consumed but the main product proved to be 2,5-diphenyl-1,3,4-thiadiazole (8) (36%). Its removal by filtration yielded a solution from which small amounts of *N*,*N*′-di-t-butylurea (15%), t-butylamine hydrochloride (6%), and a yellow solid

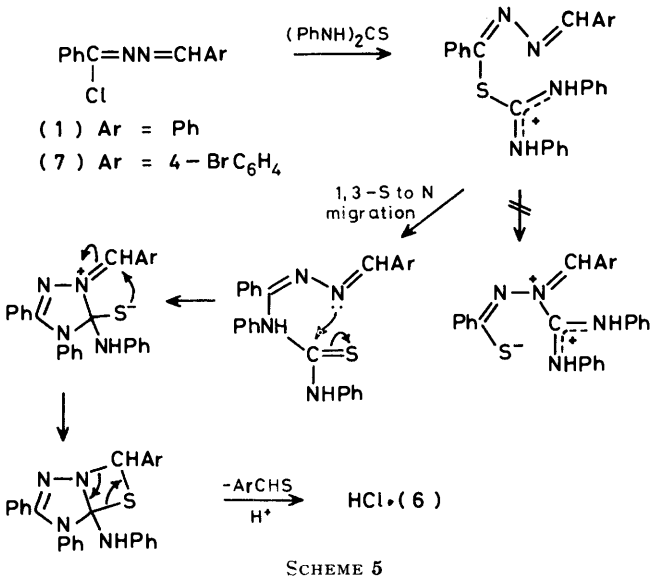


SCHEME 4

(c) *With* N,N′-*diphenylthiourea*. The effect of *N*-phenyl substitution was further explored by examining the reaction of (1) with *N*,*N*′-diphenylthiourea. Unexpectedly, the hydrochloride obtained was found to contain no sulphur and yielded a base eventually identified as 3-anilino-4,5-diphenyl-4*H*-1,2,4-triazole (6) (Scheme 3). An authentic sample of compound (6) was prepared by the known reaction of 1-benzoyl-4-phenylthiosemicarbazide with aniline.[4]

This alteration in the course of the chlorodiazabutadiene–thiourea reaction, which we believe to proceed usually by the pathway shown in Scheme 4,[1] cannot were isolated. The colour, u.v. spectrum, and ^1H n.m.r. (CH=N at δ 8.25) data of the last product indicated the presence of a diazabutadiene residue, but its ^{13}C n.m.r. spectrum also indicated a thiadiazoline ring [δ(C-5) 71.2 p.p.m.] and *three* C=N bonds (δ 135.4, 141.6, and 155.9 p.p.m.). It is identified as the diazabutadienylthiadiazoline (9) (5%), a compound which had previously been obtained in this laboratory by treatment of (1) with sodium hydrogen sulphide,[5] although its identification prior to the advent of ^{13}C n.m.r. facilities had been incomplete (Scheme 6).

The formation of these products may be rationalised on



SCHEME 5

the basis of initial nucleophilic attack by sulphur and, ring closure being obstructed by the t-butyl groups, subsequent C–S cleavage yielding an imidoylthiolate (10) which cyclizes to an *N*-anion nucleophilic enough to attack (1). The thiolate (10) is that expected to arise from compound (1) and an excess of disulphide, which reconciles this result with the earlier unpublished observation (Scheme 7).

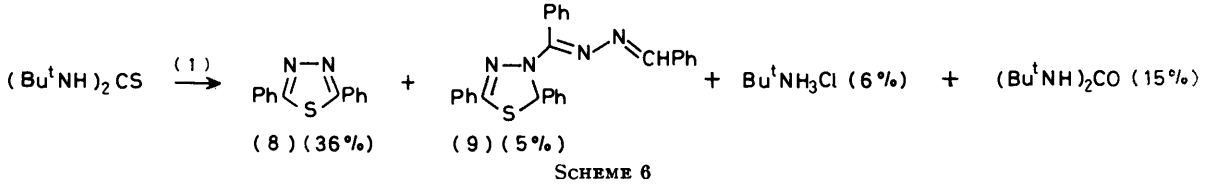
Mass Spectra of 2,5-*Diphenyl*-Δ^2-1,3,4-*thiadiazoline*-4-*carboxamidines* (2a—f).—The mass spectra of 4-aryl-Δ^2-1,3,4-thiadiazolines have been investigated systematically by Wolkoff and Hammerum,[6] and their findings enable us to rationalise the fragmentations observed in the mass spectra of the thiadiazoline-4-carboxamidines (2a—f) on the basis of two pathways (Scheme 8). The first (path A) involves the reversal of the electrocyclic ring closure proposed for the formation of these compounds,[1] and the subsequent formation of an amidoylnitrilium ion (11) leading ultimately to the abundant ions of *m/z* 103 and 104 ($PhC\overset{+}{N}$ and $PhCH\overset{+}{N}$). An alternative (path B) leads to the thiadiazolium cation (12) and thence to the observed ions of *m/z* 121 ($PhCS^+$) and 135 ($PhNCS^+$).

EXPERIMENTAL

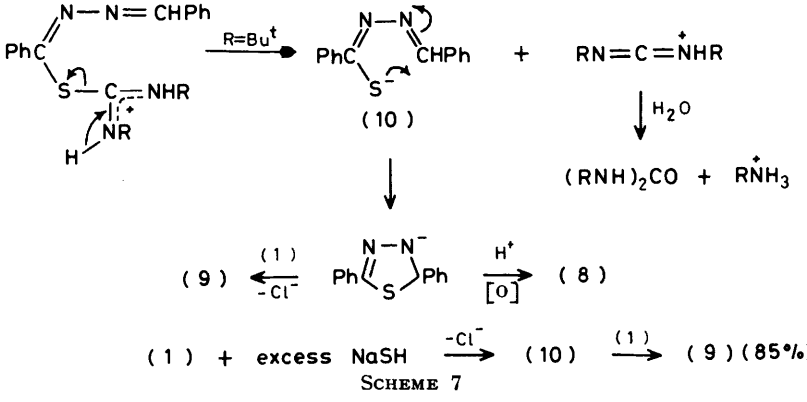
Chromatographic and spectroscopic techniques have been described previously.[1] The thioureas were obtained commercially or were prepared by the reaction of methyl isothiocyanate with the appropriate amine. 1-Chloro-1,4-diphenyl-2,3-diazabutadiene (1) was prepared by the reaction of N^1-benzoyl-N^2-benzylidenehydrazine with thionyl chloride.[7] I.r. and mass spectral results for certain compounds have been deposited as a Supplementary publication [SUP. No. 23342 (10 pages)].*

Reactions of 1-*Chloro*-1,4-*diphenyl*-2,3-*diazabutadiene* (1). —(a) *With methylthiourea.* The chlorodiazabutadiene (3.0 g, 12.4 mmol) was added in a single portion to a stirred solution of *N*-methylthiourea (1.11 g, 12.3 mmol) in anhydrous ethanol (30 cm^3) and stirring was continued for 1 h. Diethyl ether (30 cm^3) was then added to the mixture and the white precipitate which formed was filtered off, recrystallized from ethanol, and identified spectroscopically as N^1-*methyl*-2,5-*diphenyl*-Δ^2-1,3,4-*thiadiazoline*-4-*carboxamidine hydrochloride* (3.55 g, 10.7 mmol, 87%) (Found: C, 57.5; H, 5.2; Cl, 10.5; N, 16.7; S, 9.6. $C_{16}H_{17}ClN_4S$ requires C, 57.7; H, 5.2; Cl, 10.7; N, 16.8; S, 9.6%), m.p. 303 °C (with decomp.); ^{1}H n.m.r. (60 MHz, CF_3CO_2H) δ 3.10 (d, collapsing to a singlet on irradiation of the δ 6.5 region, NH*Me*, $|J|$*ca.* 5 Hz), 6.5 (br m, 3 × NH), 7.0 (s, C*H*Ph) and 7.2—8.0 (m, 2 × Ph); $\lambda_{max.}$ (EtOH) (ε values in parentheses) 318 (8 400) and 258 nm (16 500); $\lambda_{min.}$ 290 (5 700) and 238 nm (10 500). An aqueous solution of sodium

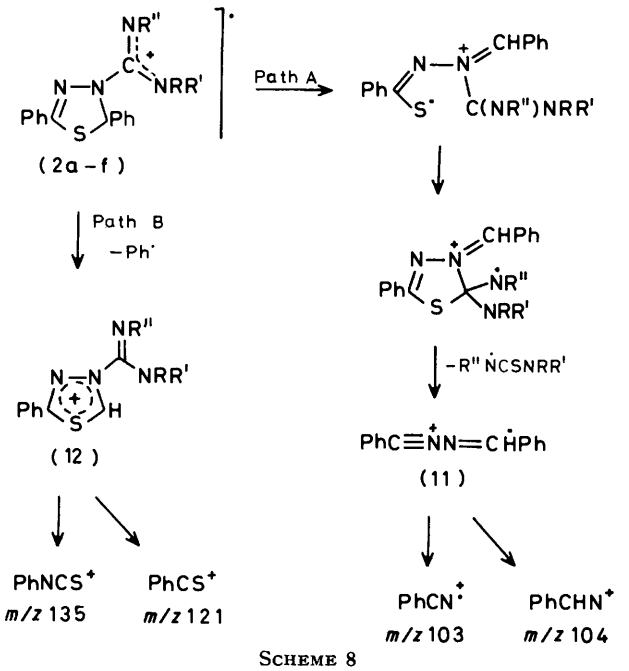
* For details of the Supplementary publications scheme, see *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.



SCHEME 6



SCHEME 7



SCHEME 8

hydroxide (1%, 120 cm³) was rapidly added to a hot stirred solution of the hydrochloride (2.80 g, 8.4 mmol) in methanol (120 cm³), and the solution was allowed to cool. The precipitate was filtered off and washed successively with water, ethanol, and diethyl ether, to give N¹-*methyl*-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline*-4-*carboxamidine* (2b) (2.18 g, 7.4 mmol, 88%) (Found: C, 6.46; H, 5.4; N, 18.9; S, 10.8%; M^+, 296. $C_{16}H_{16}N_4S$ requires C, 64.8; H, 5.4; N, 18.9; S, 10.8%; *M*, 296), m.p. 150—151 °C, ^{1}H data in Table 1, ^{13}C n.m.r. data in Table 2, and mass spectra and i.r. data in the Supplementary publication; $\lambda_{max.}$ (ε) (EtOH) 320 (7450), 295 (5 300), and 255 nm (14 950); $\lambda_{min.}$ 297 (5 250), 291 (5 200), and 238 nm (11 450).

(b) *With* N,N'-*dimethylthiourea*. A similar experiment, using the 1-chlorodiazabutadiene (1) (3.0 g, 12.4 mmol) and *N,N'*-dimethylthiourea (1.29 g, 12.4 mmol), led to the isolation of N¹,N²-*dimethyl*-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline*-4-*carboxamidine hydrochloride* (3.55 g, 10.2 mmol, 83%) (Found: C, 59.2; H, 5.7; Cl, 10.7; N, 16.0; S, 8.8%. $C_{17}H_{19}ClN_4S$ requires C, 58.9; H, 5.5; Cl, 10.2; N, 16.2; S, 9.2%), m.p. 208—209 °C (from EtOH); ^{1}H n.m.r. (60 MHz, CF_3CO_2H) δ 315 (d, collapsing to a singlet when the δ 6.5 region was irradiated, 2 × N*Me*, |*J*| *ca.* 5 Hz), 6.5 (br s, 2 × NH), 7.0 (s, C*H*Ph), and 7.20—8.00 (2 × Ph); $\lambda_{max.}$ (EtOH) (ε values in parentheses) 317 (9 250) and 254 nm (18 100); $\lambda_{min.}$ 289 (5 600) and 238 nm (13 950). Treatment of the hydrochloride (2.0 g, 5.8 mmol) in water (30 cm³) with aqueous sodium hydroxide (9%, 5 cm³) gave an oil which was extracted into chloroform (30 cm³). The extract was dried and evaporated, leaving a light-brown glass which failed to crystallize but was identified spectroscopically as N¹,N²-*dimethyl*-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline*-4-*carboxamidine* (2c) (1.8 g, 5.8 mmol, 100%) (Found: M^+, 310. $C_{17}H_{18}N_4S$ requires *M*, 310), with the spectroscopic data shown in Tables 1 and 2 and in the Supplementary publication.

(c) *With trimethylthiourea*. A similar experiment, using the 1-chlorodiazabutadiene (1) (5.0 g, 20.6 mmol) and *N,N,N'*-trimethylthiourea (2.43 g, 20.6 mmol), gave after 20 h a solution which was evaporated under reduced pressure. The yellow oily residue was dissolved in a 2 : 1 mixture (40 cm³) of carbon tetrachloride and chloroform and the solution was extracted with water (3 × 30 cm³). The combined extracts were evaporated under reduced pressure to leave an oily residue which was dissolved in dichloromethane and the solution dried ($MgSO_4$) and re-evaporated. The yellow residue was finally induced to crystallize by trituration with diethyl ether–acetone (1 : 1) to yield cream prisms identified spectroscopically as N¹,N¹,N²-*trimethyl*-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline*-4-*carboxamidine hydrochloride* (6.85 g, 19.0 mmol, 92%) (Found: C, 59.7; H, 5.9; Cl, 9.7; N, 15.8; S, 8.4. $C_{18}H_{21}ClN_4S$ requires C, 59.9; H, 5.8; Cl, 9.8; N, 15.5; S, 8.9%), m.p. 191—193 °C; ^{1}H n.m.r. (60 MHz, $CDCl_3$) δ 2.73 (d, collapsing to a singlet when irradiated at δ 10.3, NH*Me*), 3.10 (s, NMe_2), 7.2—7.9 (m, 2 × Ph), 8.1 (br s, C*H*Ph), and 10.4 (br q, collapsing to a singlet when irradiated at 2.74 p.p.m., N*H*Me); ^{13}C n.m.r. (15.1 MHz, $CDCl_3$) δ 30.8 (q in off-res., $NHCH_3$), 40.2 (q in off-res., NMe_2), 71.7 (d in off-res., *C*HPh), 126.8—137.4 (Ar × 2), 152.7 (3-C), and 155.4 p.p.m. (exocyclic C=N); $\lambda_{max.}$ (EtOH) (ε values in parentheses) 318 (11 000) and 251 nm (18 600); $\lambda_{min.}$ 287 (6 250) and 237 nm (16 000). The hydrochloride (2.0 g, 5.55 mmol) was treated as above with 4% aqueous sodium hydroxide (12 cm³) in ethanol (13 cm³). Evaporation gave an oil which was taken up in chloroform (20 cm³) and the solution washed with water (3 × 15 cm³) and dried ($MgSO_4$). Evaporation of the extract under reduced pressure gave a pale-yellow glass identified spectroscopically as N¹,N¹,N²-*trimethyl*-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline*-4-*carboxamidine* (2d) (1.80 g, 5.55 mmol, 100%) (Found: C, 66.8; H, 5.9; N, 16.9; S, 10.3. $C_{18}H_{20}N_4S$ requires C, 66.7; H, 6.2; N, 17.3; S, 9.9%), with the spectroscopic data shown in Tables 1 and 2 and in the Supplementary publication.

(d) *With phenylthiourea*. A suspension of *N*-phenylthiourea (2.50 g, 16.4 mmol) and the 1-chlorodiazabutadiene (1) (4.30 g, 17.8 mmol) in ethanol (40 cm³) was stirred at 25 °C for 20 h and then at 50—60 °C for a further 20 h. The solvent was evaporated and the residual oil stirred with methanol (15 cm³) and then diethyl ether (60 cm³); the white precipitate was recrystallized from acetone and then again from ethanol–ether to give a hydrochloride (5.80 g, 14.7 mmol, 90%), m.p. 160 °C (with decomp.); ^{1}H n.m.r. (60 MHz, [$^2H_6$]dimethyl sulphoxide) δ 7.0—8.1 (m, 3 × Ph), 8.23 (s, C*H*Ph), 8.75 (br s, NH_2), and 11.2 (N*H*Ph). A sample of the hydrochloride (2.33 g, 5.9 mmol) was treated as above with 2% aqueous sodium hydroxide (45 cm³) in ethanol (10 cm³); the mixture was extracted with chloroform (3 × 25 cm³), and the extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was recrystallized by the addition of ethanol (15 cm³) and cooling, and the precipitate was identified spectroscopically as N²,2,5-*triphenyl*-Δ²-1,3,4-*thiadiazoline*-4-*carboxamidine* (2f) (1.63 g, 4.6 mmol, 77%) (Found: C, 70.7; H, 4.8; N, 15.4; S, 8.8%; M^+, 358. $C_{21}H_{18}N_4S$ requires C, 70.4; H, 5.0; N, 15.6; S, 8.9%; *M*, 358), m.p. 121—123 °C, with the spectroscopic data shown in Tables 1 and 2 and in the Supplementary publication; $\lambda_{max.}$ (ε) (EtOH) 320 (10 300) and 256 nm (17 600), $\lambda_{min.}$ 290 (6 700) and 238 nm (14 500); λ_{inf} 297 (7 050) and 2 20 nm (18 100).

(e) *With allylthiourea*. In a similar experiment to that described for methylthiourea, the chlorodiazabutadiene (1) (5.0 g, 20.6 mmol) and *N*-allylthiourea (2.39 g, 20.6 mmol)

gave N¹-*allyl*-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline*-4-*carboxamidine hydrochloride* (6.0 g, 16.7 mmol, 81%) (Found: C, 60.5; H, 5.1; Cl, 9.7; N, 15.9; S, 9.2. $C_{18}H_{19}ClN_4S$ requires C, 60.3; H, 5.3; Cl, 9.9; N, 15.6; S, 8.9%), m.p. 247—249 °C (with decomp.); $\lambda_{max.}$ (in EtOH) (ε values in parentheses) 317 (8 600), 258 (16 550), and 217 nm (18 716); $\lambda_{min.}$ 289 (5 550) and 238 nm (10 500). The hydrochloride (2.80 g, 7.8 mmol) in hot methanol (40 cm³) was treated with aqueous sodium hydroxide (2.5%; 50 cm³), the mixture was extracted with chloroform (3 × 40 cm³), and the combined extracts were dried and evaporated to give a glass which failed to crystallize but which was identified spectroscopically as N¹-*allyl*-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline*-4-*carboxamidine* (2e) (2.52 g, 7.8 mmol, 100%) (Found: M^+, 322. Calc. for $C_{18}H_{18}N_4S$: M, 322) with the spectroscopic data shown in Tables 1 and 2 and in the Supplementary publication. Attempted molecular distillation of the glass at 180 °C/0.01 mmHg gave benzonitrile as the only distillate.

(f) *With* N,N'-*diphenylthiourea*. The 1-chloro-2,3-diazabutadiene (1) (2.20 g, 9.1 mmol) was added to a stirred suspension of *N,N'*-diphenylthiourea (2.08 g, 9.2 mmol) in ethanol (40 cm³), and the mixture was stirred for 23 h. The ethanol was evaporated under reduced pressure and the orange oily residue was then stirred with diethyl ether (50 cm³) for 5 h. The precipitate was recrystallized from acetonitrile and identified as the hydrochloride of 3-anilino-4,5-diphenyl-4*H*-1,2,4-triazole (6) (2.40 g, 6.9 mmol, 76%) (Found: C, 69.2; H, 5.2; Cl, 10.2; N, 16.4. Calc. for $C_{20}H_{17}ClN_4$: C, 68.9; H, 4.9; Cl, 10.2; N, 16.1%), m.p. 219—224 °C; ¹H n.m.r. (60 MHz, [²H₆]dimethyl sulphoxide) δ 7.3—7.8 (3 × Ph) and 9.54 (br, s, 2 × NH), with a mass spectrum identical with that of the corresponding free base (6) apart from a 100% rel. int. peak at *m/z* 36 (39% at *m/z* 38). The hydrochloride (0.53 g, 1.5 mmol) in ethanol (5 cm³) was converted by treatment with 3% aqueous sodium hydroxide (5 cm³) into 3-anilino-4,5-diphenyl-4*H*-1,2,4-triazole (6) (450 mg, 1.4 mmol, 93%) (Found: C, 76.6; H, 5.6; N, 17.6%; M^+, 312. Calc. for $C_{20}H_{16}N_4$: C, 76.9; H, 5.2; N, 17.9%; M, 312), m.p. and mixed m.p. with an authentic sample 212—213 °C (lit.,[4] m.p. 210—213 °C). The authentic sample was prepared in 10% yield by heating aniline (0.7 cm³) with 1-benzoyl-4-phenylthiosemicarbazide (2.5 g) at 170—215 °C for 3 h, and was isolated by flash chromatography ($CDCl_3$, R_F 0.28). The same triazole (6) was obtained in 91% yield from a similar reaction between *N,N'*-diphenylthiourea and 4-(4-bromophenyl)-1-chloro-1-phenyl-2,3-diazabutadiene [7] in dry ethanol at 20 °C.

(g) *With* N,N'-*di-t-butylthiourea*. The 1-chloro-2,3-diazabutadiene (1) (5.0 g, 20.6 mmol) and *N,N'*-di-t-butylthiourea (3.88 g, 20.6 mmol) were stirred at 25 °C in ethanol (50 cm³) and the precipitate was collected and identified by comparison with an authentic sample as 2,5-diphenyl-1,3,4-thiadiazole (8) (1.76 g, 7.3 mmol, 36%), m.p. and mixed m.p. with authentic material 140—141 °C (lit.,[8] m.p. 141—142 °C). The filtrate was evaporated under reduced pressure to a volume of 20 cm³ and diethyl ether was added (40 cm³). The yellow precipitate which formed was collected, recrystallized from EtOH, and identified spectroscopically as 4-(1,4-diphenyl-2,3-diazabutadien-1-yl)-2,5-diphenyl-Δ²-1,3,4-thiadiazoline (9) (430 mg, 1.0 mmol, 5%) (Found: C, 75.4; H, 5.0; N, 12.8; S, 7.2%; M^+, 446. Calc. for $C_{28}H_{22}N_4S$: C, 75.3; H, 5.0; N, 12.6; S, 7.2%; M, 446), m.p. 159—161 °C (lit.,[5] m.p. 162 °C); ¹H n.m.r. (60 MHz, $CDCl_3$) δ 7.2—7.7 (m, 4 × Ph) and 8.25 p.p.m. (s, =C*H*Ph) (the thiadiazoline C(5) *H* methine is presumed to be masked by the aromatic resonances); ¹³C n.m.r. (20 MHz) δ 71.2 (*C*HPh), 126.3—132.2 (4 × C_6H_5), 135.4 and 141.6 (2 × C=N), and 155.9 p.p.m. (N=*C*HPh); $\lambda_{max.}$ (EtOH) (ε in parentheses) 370 (33 350) and 232 nm (27 200); $\lambda_{min.}$ 291 (10 550) and 219 nm (25 100); *m/z* (rel. int. as % base peak) 446 (1%, M^+), 311 (4%), 310 (6%), 240 (19%), 239 (100%), 222 (12%), 135 (30%), 121 (24%), 105 (29%), 104 (99%), 103 (33%), and 77 (73%). The filtrate was evaporated under reduced pressure and the oily residue was purified by elution

TABLE 1

¹H N.m.r. data for the Δ²-1,3,4-thiadiazoline-4-carboxamidines (2) in $CDCl_3$

Compd.	R	R'	R''	δ of assigned resonances: NH	NH_2	NMe	C*H*Ph	Aromatics
(2a)	H	H	H	4.5 (br)	4.5 (br)	—	7.02	7.15—7.74
(2b)	Me	H	H	4.78 (br)	—	2.78 (3 H)	7.10	7.18—7.80
(2c)	Me	H	Me	4.3 (br)	—	2.90 (6 H)	7.05	7.14—7.80
(2d)	Me	Me	Me	—	—	2.73 (6 H) 2.94 (3 H)	*a*	7.10—7.90
(2e)	Allyl [b]	H	H	5.1 (br)	—		7.11	6.90—7.75
(2f)	H	H	Ph	—	4.87 (br)		*a*	6.45—7.75

[a] Masked by resonances due to phenyl groups. [b] Allyl-group protons: 3.5—3.8 (NCH_2), 5.6—6.0 (=CH), and 4.9—5.3 ($=CH_2$).

TABLE 2

¹³C N.m.r. data for the Δ²-1,3,4-thiadiazoline-4-carboxamidines (2) in $CDCl_3$

Compd.	R	R'	R''	δ (p.p.m) (off-resonance multiplicity in parentheses) [a]: C-1	C-2	C-3	C4	NMe	NMe_2
(2a)	H	H	H	141.5	70.5 (d)	145.9	154.5		
(2b)	Me	H	H	142.0	70.5 (d)	145.2	155.0	28.3 (q)	
(2c)	Me	H	Me	140.3	71.0 (d)	144.1	150.9	32.3 (q)	
(2d)	Me	Me	Me	138.8	72.3 (d)	146.1	153.3	34.4 (q)	35.7 (q)
(2e)	Allyl [b]	H	H	141.7	70.2 (d)	145.1	153.0		
(2f)	H	H	Ph	138.3	69.6	152.2	155.1		

[a] Remaining aromatic carbons in the range 125—130 p.p.m. [124—134 in compound (2f)]. [b] Allyl-group carbons at 44.6 (t) (NCH_2), 134.6 (d) (CH=), and 115.3 (t) p.p.m. ($=CH_2$).

through Merck silica gel 60 with $CHCl_3$ (700 cm^3) giving *N,N'*-di-t-butylurea (540 mg, 3.1 mmol, 15%) (Found: C, 62.5; H, 11.9; N, 16.0. Calc. for $C_9H_{20}N_2O$: C, 62.8; H, 11.7; N, 16.3%), m.p. 240 °C (lit.,[9] m.p. 240 °C). Further elution of the column with $CHCl_3$–MeOH (5 : 2) (500 cm^3) gave t-butylamine hydrochloride (270 mg, 2.5 mmol, 6% based on di-t-butylthiourea) m.p. and mixed m.p. with an authentic sample 304 °C (with decomp.) (lit.,[10] m.p. 291 °C, with decomp.).

We thank Reckitt and Colman Ltd, Pharmaceutical Division, Hull, for financial assistance (to S. F. M.) and helpful discussions.

[1/1727 *Received*, 9*th November*, 1981]

REFERENCES

[1] Part 1, S. H. Askari, S. F. Moss, and D. R. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1981, 360.
[2] A. R. Katritzky and J. M. Lagowski, *Adv. Heterocycl. Chem.*, 1963, **1**, 336.
[3] D. C. Prevorsek, *J. Phys. Chem.*, 1962, **66**, 769.
[4] W. Dymek, *Ann. Univ. Mariae Curie-Sklodowska, Sect. AA*, 1954, **9**, 61 (*Chem. Abstr.*, 1957, **51**, 5095b).
[5] W. T. Flowers, J. F. Robinson, D. R. Taylor, and A. E. Tipping, unpublished observations; J. F. Robinson, Ph.D. Thesis, U.M.I.S.T., 1978.
[6] P. Wolkoff and S. Hammerum, *Org. Mass Spectrom.*, 1974, **9**, 181.
[7] W. T. Flowers, J. F. Robinson, D. R. Taylor, and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1*, 1981, 349.
[8] R. Stollé and K. Thoma, *J. Prakt. Chem.*, 1906, **73**, 208.
[9] B.P. 818 864/1959 (*Chem. Abstr.*, 1960, **54**, 9774d).
[10] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, vol. 1, 4th edn., p. 511.