# Thiadiazoles and Thiadiazolines. Part 3.[1] Synthesis of Triazol-3-yl-Δ²-1,3,4-thiadiazolines and a New Synthesis of Unsymmetrical 2,5-Di-substituted 1,3,4-Thiadiazoles

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The reaction of 1-chloro-1,4-diphenyl-2,3-diazabutadiene (1) with 1-acetyl- and with 1-benzoyl-thiosemicarbazide yields initially the hydrochlorides of N^2-acetyl- and N^2-benzoyl-Δ²-1,3,4-thiadiazoline-4-carboxamide hydrazone (4a, b) which are converted by aqueous sodium hydroxide into the corresponding free bases (5a, b) and thence by cyclodehydration into 4-(4H-1,2,4-triazol-3-yl)-Δ²-1,3,4-thiadiazolines (6a, b). Treatment of (1) with thioacetamide, thionicotinamide, or the thiobenzamides 4-$XC_6H_4CSNH_2$ (where X = H, MeO, and Cl), leads at 20—95 °C to 2-phenyl-5-R-1,3,4-thiadiazoles (9a—e) (where R = Me, 3-pyridyl, or 4-XC_6H_4). The reaction of (1) with guanidine leads, via the hydrochloride, to 3-amino-5-phenyl-4H-1,2,4-triazole. The mechanism of these and related reactions of (1) with other S-nucleophiles are discussed.

IN preceding publications [1-3] we have reported two distinct ways in which 1-chloro-2,3-diazabutadienes such as (1) react with compounds containing the NH·CS·NH grouping (Scheme 1). Thus, thioureas and (1) react rapidly at ambient temperature to yield hydrochlorides of Δ²-1,3,4-thiadiazoline-4-carboxamidines [2; $R^1 =$ $R^2 =$ H or Me; $R^1R^2 =$ -$(CH_2)_2$-; $R^1 =$ H, $R^2 =$ Me, Ph, or allyl]. In contrast, thiosemicarbazide and
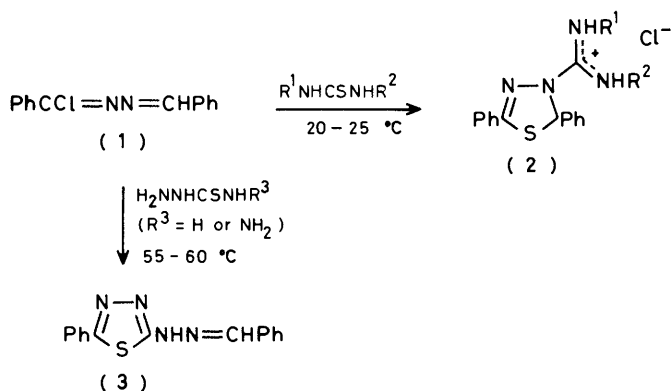
SCHEME 1

thiocarbohydrazide react with compound (1) at 55—60 °C to produce the thiadiazolylhydrazone (3), a reaction which is unaffected by substitution in either or both of the phenyl groups. This difference in behaviour, which follows from the presence or absence of at least one additional NH group in the S-nucleophile attacking (1), appeared sufficiently interesting to be investigated further by new variations in the structure of the nucleophile. We now report the results of the study of reactions of (1) with (a) acylthiosemicarbazides (RCON-HNHCSNH₂, where R = Me or Ph) in which the nucleophilicity of the additional NH₂ group has been reduced by an adjacent carbonyl group, (b) thioamides, in which only one NH₂ group is present, and (c) guanidine, in which the fragile C–S bond has been altered to the stronger C–N bond.

Reactions of 1-Chloro-1,4-diphenyl-2,3-diazabutadiene (1).—(a) *With acylthiosemicarbazides.* When 1-acetyl- and 1-benzoyl-thiosemicarbazide[4] were separately treated with the chlorodiazabutadiene (1) at ambient temperature, hydrochlorides were formed which were readily converted into the corresponding bases with aqueous sodium hydroxide. These bases displayed the characteristic spectroscopic features [1,2] of 4-substituted Δ²-1,3,4-thiadiazolines (5a, b), namely a ¹H n.m.r. resonance at δ 7.07 [in (5a) only, this signal being hidden by the aromatic proton resonances in (5b)] and a ¹³C resonance [71.0 p.p.m. in (5a), 69.7 p.p.m. in (5b)] which appears as a doublet in the off-resonance spectrum, attributable to the 5-methine group. These features are quite incompatible with an acyclic imine structure.

On melting, compounds (5a, b) were observed to re-solidify and then, at a substantially higher temperature, re-melt, behaviour which suggests the occurrence of a facile cyclodehydration, a well-known property of acylamidrazones.[5] This was confirmed on a preparative scale using a Dean and Stark separator to remove the water azeotropically with toluene; the dehydration of (5b) was also assisted by the addition of toluene-*p*-sulphonic acid monohydrate. The products of the dehydration were isolated in almost quantitative yield and were identified spectroscopically as the novel 4-triazol-3-yl-Δ²-1,3,4-thiadiazolines (6a, b) (Scheme 2). The presence of the thiadiazoline ring in these compounds was confirmed as before by the characteristic n.m.r. resonances [*e.g.* δ$_C$ 72.5—72.6 p.p.m., doublets in the off-resonance spectra], which are only marginally affected by the aromatization of the 4-substituent; these values may be compared with those of analogous 4-phenylthiadiazolines first prepared by Wuyts and Lacourt[6] (δ$_H$ 6.83, δ$_C$ 73.2 p.p.m.[7]).

The formation of 4-substituted Δ²-thiadiazolines from the interaction of compound (1) with these deactivated thiosemicarbazides parallels the behaviour of (1) with substituted thioureas,[1,3] suggesting that the presence of a nucleophilic, unsubstituted, 1-nitrogen as in thio-

semicarbazide and thiocarbohydrazide is necessary if such reactions of (1) are to lead to thiadiazoles [3] rather than to thiadiazolines.

(b) *With thioamides.* This study was undertaken in the expectation that an analogous reaction to that occurring between compound (1) and thioureas would occur,

SCHEME 2
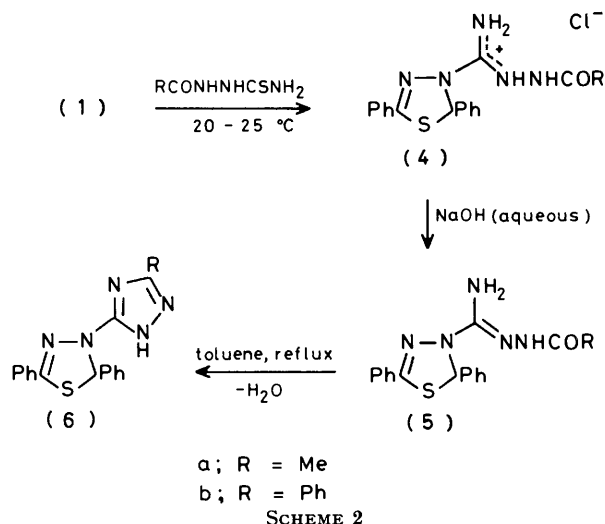
leading to 4-acyl-Δ^2-1,3,4-thiadiazolines (7) by hydrolysis of the intermediate iminium salts (8). We have since devised other routes to 4-acylthiadiazolines of this type; [8] 4-acyl-2-acylamino- and 4-acyl-2-amino-Δ^2-1,3,4-thiadiazolines have also been reported recently by Kubota and his co-workers, who obtained them by acylation of thiosemicarbazones. [9]

The chlorodiazabutadiene (1) reacted smoothly and rapidly with thiobenzamide at ambient temperature to give a mixture of ammonium chloride and 2,5-diphenyl-1,3,4-thiadiazole (9a) (74%). Because (9a) is a product we have frequently obtained on treatment of (1) or the related 1,4-dichloro-1,4-diphenyl-2,3-diazabutadiene with S-nucleophiles, [1,10,11] it was necessary to establish which of the three phenyl groups had been eliminated in its formation from thiobenzamide. Accordingly, two 4-substituted thiobenzamides were prepared and their reactions with compound (1) investigated. The only thiadiazoles detected in the reaction products were (9b, c), in which the 4-substituted phenyl group from the thiobenzamide has been retained, confirming the formulation of the reaction presented in Scheme 3.

The effect of rendering the thiobenzamide less nucleophilic was tested using thionicotinamide; the reaction took the same course, yielding (9d) (61%), although a higher temperature proved necessary to achieve complete reaction. The chlorodiazabutadiene (1) also reacted more slowly with thioacetamide, giving ammonium chloride (63%) and three organic products detectable by t.l.c. Only one of these was isolated; it was identified as 2-methyl-5-phenyl-1,3,4-thiadiazole (9e) (28%).

These experiments, together with the outcome of

SCHEME 3
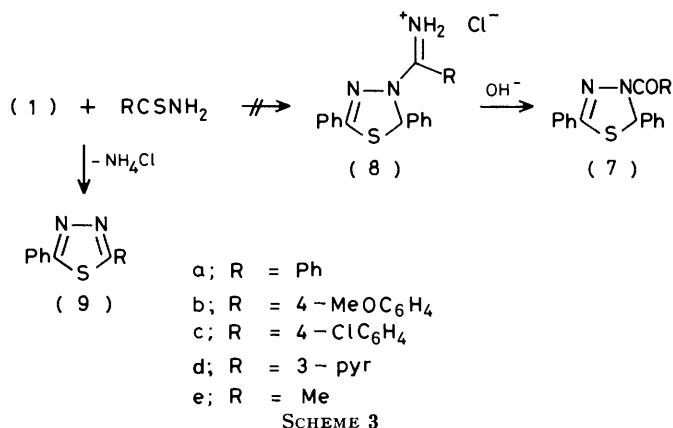
reactions of 1-chloro-diazabutadienes such as (1) with potassium thiocyanate and other S-nucleophiles, [3] indicate that the presence of the NH·CS·NH or the related NH·CS·NHCOR grouping is essential if ring closure to a Δ^2-thiadiazoline is to occur. The reaction of (1) with thioamides also affords an alternative to previously reported syntheses of unsymmetrically substituted 1,3,4-thiadiazoles. [12-14]

(c) *With guanidine.* The expected product, based on the previously studied reaction of (1) with thioureas, [1,2] was the 4,5-dihydro-1,2,4-triazole-1-carboxamidinium chloride (10). The reaction proved much more difficult to follow than those described earlier, since the product was not visible on t.l.c. plates under u.v. light at 254 nm, and iodine-staining was necessary. The product was converted into a very water-soluble hydrochloride which was isolated in 48% yield and identified spectroscopically and from its m.p. as the hydrochloride of 3-amino-5-phenyl-4H-1,2,4-triazole (11), from which the free triazole [15] was liberated by aqueous hydroxide (Scheme 4).
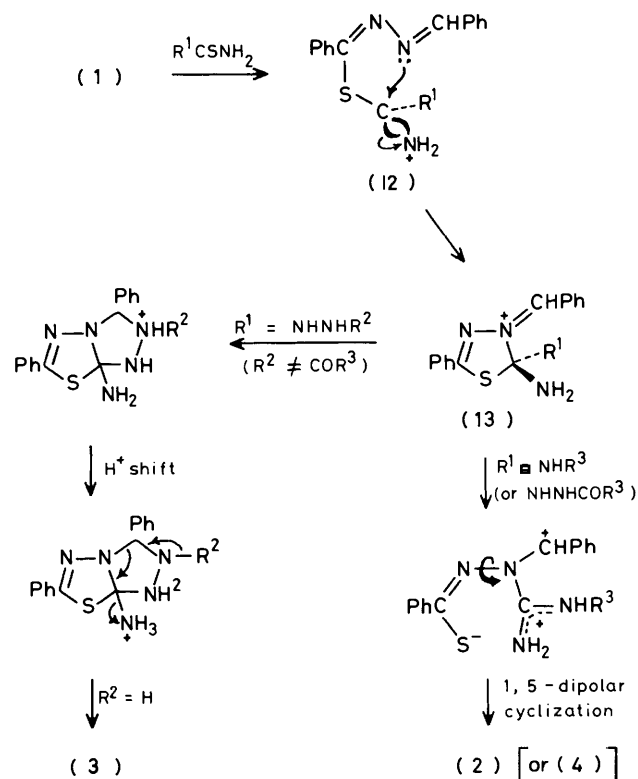
SCHEME 4
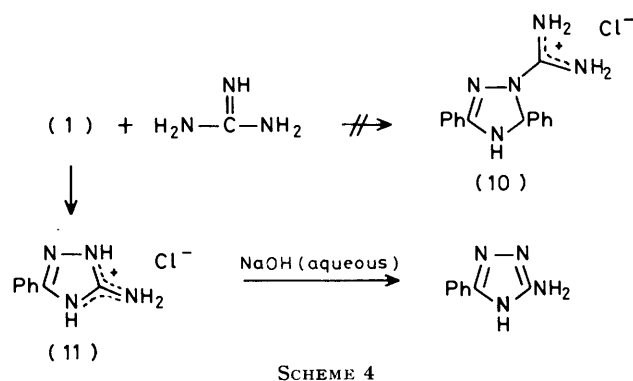
Removal of the weak C–S bond in the nucleophile, like the presence of steric hindrance to ring closure found in reactions of compound (1) with diphenyl- and di-t-butyl-thiourea, [1] evidently inhibits 4,5-dihydrotriazole formation.

Mechanism of the Reactions of Compound (1) *with S-Nucleophiles.*—All aspects of the chemistry of 1-

chlorodiazabutadienes such as (1) are consistent with a pronounced susceptibility to nucleophilic displacement of chloride and, since 1,4-diphenyl-2,3-diazabutadiene (benzaldehyde azine) is unreactive towards S-nucleophiles,[3] we propose initial S-imidoylation by (1) to give intermediates of the general structure (12) (Scheme 5) as the only reasonable common step in reactions of (1) with thioureas, thioamides, and thiosemicarbazides. Molecular models show that when the $R^1C=\overset{+}{N}H_2$ unit in (12) is perpendicular to the plane of the diazabutadiene moiety, the 3-nitrogen is well-placed to accomplish a 5-exo-trigonal ring closure in accord with Baldwin's Rules,[16] leading to the 4-benzylidenethiadiazolium ion (13). At this juncture the nature of R^1 is evidently critical.

When R^1 is a nucleophilic $NHNHR^2$ unit (e.g. $R^2 =$ H), a second ring closure must occur by attack upon the 4-iminium ion, leading eventually to the thiadiazolylhydrazones (3). Terminal acylation ($R^2 = COR^3$) effectively blocks this pathway; an interesting experiment we have yet to perform is to test the effect of increasing the nucleophilicity of the terminal nitrogen (e.g. with R^2 = alkyl), since this would have the secondary effect of inhibiting the subsequent ring-opening which produces (3).

When R^1 is NHR^3 or $NHNHCOR^3$, the favoured pathway is that leading via C–S fission, rotation about the N–N bond, and a 1,5-dipolar electrocyclic rearrangement,[17] to protonated Δ^2-1,3,4-thiadiazoline-4-carboxamidines (2) or -carboxamide hydrazones (4) (Schemes 1—2). Much more difficult to explain is the reaction of compound (1) with thioamides ($R^1 =$ Me or Ar). Formation of an additional four- rather than a five-membered ring (Scheme 6, path A) is an attractive possibility, but it appears to require a symmetry-forbidden retro-cycloaddition, and we accordingly propose that the decomposition of either the protonated bicyclic intermediate (14) (Scheme 6, path B) or of

Scheme 5

(13; $R^1 =$ Me or Ar) (Scheme 6, path C) is initiated by solvent ethanol.

EXPERIMENTAL

Chromatographic and spectroscopic techniques have been described elsewhere.[2] N.m.r. data were obtained using $CDCl_3$ solutions unless stated otherwise; ^{1}H spectra were obtained at 60 MHz, and ^{13}C spectra at 20 MHz. 1-Chloro-1,4-diphenyl-2,3-diazabutadiene (1) was prepared by the chlorination of N^1-benzoyl-N^2-benzylidenehydrazine
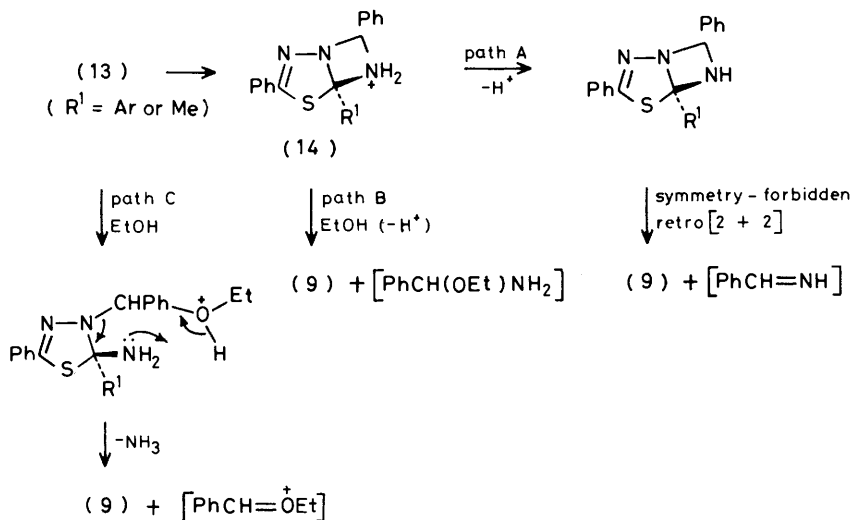
Scheme 6

using thionyl chloride.[3] 1-Acylthiosemicarbazides were prepared by treating thiosemicarbazide with the corresponding acid or acid chloride in pyridine.[4] The thiobenzamides were prepared by treating the corresponding benzonitriles with hydrogen sulphide.[18] **CAUTION** Thioacetamide is a potential carcinogen and should be handled with great caution. I.r. and mass spectral results for certain compounds have been deposited as a Supplementary publication [Sup. No. 23343 (6 pages)].*

Reactions of 1-Chloro-1,4-diphenyl-2,3-diazabutadiene (1).—(a) *With 1-acetylthiosemicarbazide.* The chlorodiazabutadiene (1) (8.54 g, 35.3 mmol) was added in a single portion to a stirred suspension of 1-acetylthiosemicarbazide (4.69 g, 35.3 mmol) in anhydrous ethanol (100 cm³), and after 22 h the solvent was evaporated. The residual oil was stirred with chloroform (50 cm³) and the cream coloured precipitate was recrystallized from a 1 : 2 mixture of ethanol and diethyl ether giving the *hydrochloride* (4a) (6.40 g, 17.1 mmol, 48%), m.p. 182—184 °C (Found: C, 53.6; H, 5.1; Cl, 9.5; N, 18.2; S, 8.5. $C_{17}H_{18}ClN_5OS$ requires C, 54.3; H, 4.8; Cl, 9.4; N, 18.6; S, 8.5%). A hot aqueous solution of sodium hydroxide (3.3%, 75 cm³) was added to a stirred solution of the hydrochloride (4a) (6.35 g, 16.9 mmol) in methanol (60 cm³) and the precipitated yellow solid was identified spectroscopically as N^2-*acetyl-2,5-diphenyl-Δ^2-1,3,4-thiadiazoline-4-carboxamide hydrazone* (5a) (5.38 g, 15.8 mmol, 45% overall yield) (Found: C, 59.9; H, 5.0; N, 20.7; S, 9.2%; M^+, 339. $C_{17}H_{17}N_5OS$ requires C, 60.2; H, 5.1; N, 20.6; S, 9.5%; M, 339), m.p. 146—148 °C; δ_H 9.75 (br and exchanged in D_2O, NHAc), 7.88—7.35 (m, 10H, Ph × 2), 7.07 (s, CHPh), 5.87 (br and exchanged in D_2O, NH₂), and 1.80 (s, COMe); δ_C 173.3 (CO), 147.3 (exocyclic C=N), 145.5 (C-2), 142—126 (Ar), 71.0 (C-5), and 19.3 p.p.m. (CH₃); i.r. and mass spectral data are given in the Supplementary publication.

(b) *With 1-benzoylthiosemicarbazide.* A similar reaction between the chlorodiazabutadiene (1) (2.0 g, 8.3 mmol) and 1-benzoylthiosemicarbazide (1.61 g, 8.3 mmol) yielded the *hydrochloride* (4b) (1.70 g, 3.9 mmol, 47%) (Found: C, 60.1; H, 4.9; N, 16.0; S, 7.3%. $C_{22}H_{20}ClN_5OS$ requires C, 60.3; H, 4.6; N, 16.0; S, 7.3%), m.p. (from ethanol–ether, 1 : 1) 225—226 °C (with decomp.). Basification of the hydrochloride (600 mg) with aqueous sodium hydroxide (3%; 7 cm³) in methanol (11 cm³) yielded a precipitate identified spectroscopically as N^2-*benzoyl-2,5-diphenyl-Δ^2-1,3,4-thiadiazoline-4-carboxamide hydrazone* (5b) (500 mg, 1.25 mmol, 43% overall yield) (Found: C, 65.9; H, 4.7; N, 17.4; S, 7.7%; M^+, 401. $C_{22}H_{19}N_5OS$ requires C, 65.8; H, 4.8; N, 17.4; S, 8.0%; M, 401), m.p. 187 °C (with decomp.); δ_H ([²H₆]dimethyl sulphoxide = [²H₆]-DMSO]) 9.82 (br and exchanged in D_2O, NHCO), 7.97—7.07 (16H, 3 × Ph and CHPh), and 4.41 (br and exchanged in D_2O, NH₂); δ_C ([²H₆]-DMSO) 196.3 (CO), 152.7 (exocyclic C=N), 144.7 (C-2), 142.3—125.5 (Ar) and 69.7 p.p.m. (C-5) (mass spectral and i.r. data in the Supplementary publication).

(c) *With thioacetamide.* The chlorodiazabutadiene (1) (5.0 g, 20.7 mmol) and thioacetamide (**CAUTION,** potential carcinogen; 1.55 g, 20.7 mmol) were stirred in dry ethanol (25 cm³) at 50 °C for 5 h and then at ambient temperature for 15 h. The precipitate was collected and identified as

* For details of the Supplementary publications scheme see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

ammonium chloride (700 mg, 63%). The filtrate was shown by t.l.c. (CHCl₃) to contain three components [R_F = 0.68 (major), 0.84 (minor), and 0.88 (minor)]. The major component was isolated by evaporation and extraction with chloroform (30 cm³). The CHCl₃ extract was washed with an equal volume of water, dried, and evaporated to give 2-methyl-5-phenyl-1,3,4-thiadiazole (9e) (1.0 g, 5.7 mmol, 28%) (Found: C, 61.4; H, 4.4; N, 15.9; S, 17.9%; M^+, 176. Calc. for $C_9H_8N_2S$: C, 61.3; H, 4.6; N, 15.9; S, 18.2%; M, 176), m. p. 105—106 °C (lit.,[12] m.p. 104—106 °C); δ_H 8.08—7.25 (Ph) and 2.78 (s, Me).

(d) *With thiobenzamides.* The 1-chlorodiazabutadiene (1) (2.0 g, 8.3 mmol) was added rapidly to a stirred solution of thiobenzamide (1.14 g, 8.3 mmol) in ethanol (30 cm³). After 20 h at room temperature the mixture was cooled and the precipitate was collected and identified as 2,5-diphenyl-1,3,4-thiadiazole (9a) (1.45 g, 6.1 mmol, 74%), m.p. and mixed m.p. with an authentic sample [3] 140—141 °C (lit.,[19] m.p. 141—142 °C).

Similarly were prepared (i) 2-(4-methoxyphenyl)-5-phenyl-1,3,4-thiadiazole (9b) (73%) (Found: C, 67.1; H, 4.6; N, 10.6; S, 12.2%; M^+, 268. Calc. for $C_{15}H_{12}N_2OS$: C, 67.1; H, 4.5; N, 10.4; S, 11.9%; M, 268), m.p. 143—144 °C (EtOH) (lit.,[12] m.p. 134—136 °C), δ_H 8.15—6.96 (Ar) and 3.82 (s, OMe); (ii) 2-(4-chlorophenyl)-5-phenyl-1,3,4-thiadiazole (9c) (63%) (Found: C, 61.4; H, 3.1; Cl, 13.1; N, 10.1; S, 11.6%; M^+, 272, 274. Calc. for $C_{14}H_9{}^{35}ClN_2S$: C, 61.7; H, 3.3; Cl, 13.0; N, 10.2; S, 11.8%; M, 272), m.p. 183—184 °C (EtOH) (lit.,[13] m.p. 183—184 °C); and (iii) 2-pyridin-3-yl-5-phenyl-1,3,4-thiadiazole (9d) (61%; an additional 4 h at reflux was required to complete this reaction) (Found: C, 65.4; H, 3.7; N, 17.6; S, 13.5%; M^+, 239. Calc. for $C_{13}H_9N_3S$: C, 65.3; H, 3.8; N, 17.6; S, 13.4%; M, 239), m.p. 153—154 °C (EtOH) (lit.,[13] m.p. 154—155 °C), δ_H 9.20, 8.74, 8.38, and 7.7 (pyr) and 8.2—7.3 (Ph).

(e) *With guanidine.* Guanidine was liberated from its carbonate (7.92 g, 44 mmol) in aqueous solution (25 cm³) by adding a standard aqueous solution of barium hydroxide (46 mmol). Ethanol was added, the solution was filtered to remove BaCO₃ (100%), and the filtrate was evaporated to an oil which was further dried by azeotropic distillation with benzene (20 cm³). The chlorodiazabutadiene (1) (8.0 g, 33.1 mmol) was added to a stirred solution of the guanidine (1.95 g, 33.1 mmol) in anhydrous ethanol (130 cm³), and the mixture was stirred for 12 h at 20—25 °C and then evaporated under reduced pressure. The oily residue was taken up in chloroform (50 cm³) and washed with an equal volume of water, the aqueous washings being back-extracted with chloroform (3 × 25 cm³). The combined CHCl₃ layers were finally extracted with aqueous hydrochloric acid (2M; 10 × 50 cm³) and the acid extract was evaporated to give, after recrystallization from ethanol, the hydrochloride of 3-amino-5-phenyl-4H-1,2,4-triazole (11) (3.10 g, 15.8 mmol, 48%), m.p. 252 °C (lit.,[20] m.p. 253—254 °C), δ_H ([²H₆]-DMSO) 8.45 (br and exchanged in D_2O, $\overset{+}{N}H_2$), 8.05—7.65 (Ph), and 6.80 (br and D_2O labile, NH × 2). The hydrochloride was dissolved in aqueous sodium hydroxide (2M; 25 cm³) and the solution was extracted with ethyl acetate (7 × 12 cm³) to give, after evaporation of the dried EtOAc extract and recrystallization of the residue from acetonitrile, 3-amino-5-phenyl-4H-1,2,4-triazole (700 mg, 4.4 mmol, 13% overall yield from chlorodiazabutadiene) (Found: C, 59.8; H, 5.1; N,

34.7%; M^+, 160. Calc. for $C_8H_8N_4$: C, 60.0; H, 5.0; N, 35.0%; M, 160), m.p. 184—185 °C (lit.,[16] m.p. 186 °C), δ_H ([$^2H_6$] DMSO) 12.27 (br and D_2O-labile, NH), 8.17—7.29 (Ph), and 6.03 (br and D_2O-labile, NH_2); $\lambda_{max.}$ (EtOH) 257 nm (ε 9 100); $\lambda_{min.}$ 241 nm (ε 7 100).

Cyclodehydrations.—(a) *Of N²-acetyl-2,5-diphenyl-Δ²-1,3,4-thiadiazoline-4-carboxamide hydrazone* (5a). A solution of the thiadiazoline (5a) (1.60 g, 4.7 mmol) in toluene (50 cm³) was heated under reflux in a Dean–Stark apparatus for 24 h. Evaporation under reduced pressure gave a solid identified spectroscopically as 4-(5-*methyl*-4H-1,2,4-*triazol*-3-*yl*)-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline* (6a) (1.50 g, 4.7 mmol, 99%) (Found: C, 63.4; H, 4.5; N, 21.9; S, 10.0%; M^+, 321. $C_{17}H_{15}N_5S$ requires C, 63.5; H, 4.7; N, 21.8; S, 10.0%; M, 321), m.p. (MeCN) 202—203 °C; δ_H ([$^2H_6$]-DMSO) 13.02 (br D_2O-labile, NH), 7.87—7.21 (10 H, Ph × 2), 7.12, (C*H*Ph), and 2.15 (Me); δ_C ([$^2H_5$]-DMSO) 141.5—125.8 (Ar and C=N), 72.5 (d in off-resonance spectrum, C*H*Ph), and 12.3 (CH_3); $\lambda_{max.}$ (EtOH) 343 (ε 8 950) and 229 nm (ε 17 850); $\lambda_{min.}$ 303 (ε 4 900), and λ_{inf} 294 (ε 5 100) and 282 nm (ε 5 700); mass spectral and i.r. data in the Supplementary publication.

(b) *Of* N²-*benzoyl-2,5-diphenyl-Δ²-1,3,4-thiadiazoline-4-carboxamide hydrazone* (5b). A suspension of the thiadiazoline (5b) (1.65 g, 4.1 mmol) and toluene-*p*-sulphonic acid monohydrate (100 mg) in toluene (75 cm³) was heated under reflux in a Dean–Stark apparatus for 24 h. Evaporation under reduced pressure gave a cream solid identified spectroscopically as 4-(4-*phenyl*-4H-1,2,4-*triazol*-3-*yl*)-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline* (6b) (1.54 g, 4.9 mmol, 98%) (Found: C, 68.7; H, 4.3; N, 18.3; S, 8.4%; M^+, 383. $C_{22}H_{17}N_5S$ requires C, 68.9; H, 4.5; N, 18.3; S, 8.4%; M, 383), m.p. (EtOH) 226—227 °C; δ_H ([$^2H_6$]-DMSO) 13.45 (br D_2O-labile, NH) and 7.95—7.15 (16 H, 3 × Ph and C*H*Ph); δ_C ([$^2H_6$]-DMSO) 159.2 and 154.0 (triazolyl C=N) 147.6 (C-2), 141.2—125.8 (Ar) and 72.6 p.p.m. (d in off-res. spectrum, C*H*Ph); $\lambda_{max.}$ (EtOH) 345 (ε 10 300) and 239 nm (ε 31 800); $\lambda_{min.}$ 311 (ε 6 350) and 216

nm (ε 19 450); λ_{inf} 279 nm (ε 9 350); i.r. and mass spectral data in the Supplementary publication.

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