Thiadiazoles and Thiadiazolines. Part 1. Reaction of Thiourea and Ethylenethiourea with Chlorodiazabutadienes: a New Route to 4-Amidino-1,3,4-thiadiazolines

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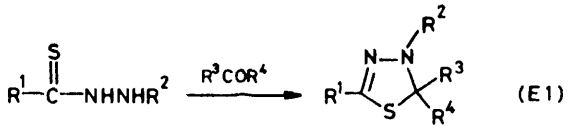
1-Chloro-1,4-diaryldiazabutadienes (1) react with thiourea to give hydrochlorides of 4-amidino-2,5-diaryl-Δ^2-1,3,4-thiadiazolines from which the corresponding free bases (2) are obtained by treatment with cold alkali. Imidazolidine-2-thione (ethylenethiourea) reacts similarly with the chlorodiazabutadienes (1a,b) to give, after treatment with cold alkali, 4-(4,5-dihydroimidazolin-2-yl)-2,5-diaryl-Δ^2-1,3,4-thiadiazolines (6a,b). In the presence of an excess of sodium borohydride the reaction of (1a) with thiourea yielded some *N*^{2}-benzylthiobenzoylhydrazine (12), compatible with the capture of an intermediate iminium ion. A mechanism is suggested for these reactions.

THIS paper is the first in a series which will report new methods for the synthesis of 1,3,4-thiadiazoles and Δ^2-1,3,4-thiadiazolines. The chemistry of 1,3,4-thiadiazoles has been covered thoroughly to 1967 in a review,[1] and recent developments have since been reviewed intermittently.[2] There is only one substantial review of Δ^2-1,3,4-thiadiazolines, and it deals only with the earliest group of publications.[3]

There are few general routes to 1,3,4-thiadiazolines. Wuyts and co-workers [4] and more recently Holmberg [5] and Sandström [6] have established that the treatment of aldehydes or ketones with *N*^{2}-substituted thiohydrazides is a facile general method for preparing 2,4- and 2,4,5-substituted Δ^2-1,3,4-thiadiazolines [equation (E1)]. Although many of these thiadiazolines were reported to display fascinating properties such as extremely high molecular rotations and formation of penta- or heptaiodides, such compounds have been little studied, and in particular no spectroscopic data have been reported.



(E1)

The only other general method for the preparation of thiadiazolines of this type appears to be the 1,3-dipolar cycloaddition of thiones to nitrilimines, a method which has not been widely exploited.[7] There are, however, alternative methods for the synthesis of iminothiadiazolines and thiadiazolones.[3] Our discovery of a general synthesis of 4-amidino-Δ^2-thiadiazolines (2) was an accident; it occurred during an investigation [8] of reactions between chlorodiazabutadienes and sulphur-nucleophiles, when thiourea was selected as the nucleophile.

RESULTS AND DISCUSSION

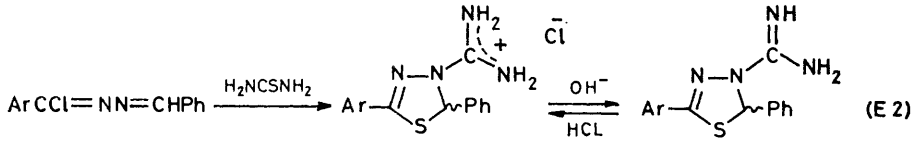
Reaction of Thiourea with Chlorodiazabutadienes.—1-Chloro-2,3-diazabutadienes (1) are very susceptible to nucleophilic attack, resembling in this respect imidoyl halides. The chloride (1a) was found to react quite rapidly with thiourea at ambient temperature in dry ethanol, a 1 : 1 adduct being easily isolated by crystallization from ethanol. The adduct had the properties of a hydrochloride but did not behave like a thiouronium salt; on treatment with aqueous ethanolic sodium hydroxide it rapidly liberated the corresponding free base in 68% overall yield. Furthermore, the hydrochloride was regenerated when the base was treated with hydrogen chloride.

The free base, $C_{15}H_{14}N_4S$, m.p. 163—164 °C (decomp.) was initially believed to be a dihydrothiatriazepine (3),[9] but further investigations, culminating in an *X*-ray crystallographic analysis already reported,[10] revealed that the base was in fact 4-amidino-2,5-diphenyl-Δ^2-1,3,4-thiadiazoline (2a) [equation (E2)].

The characteristic spectroscopic features which may in future be used to recognize such Δ^2-1,3,4-thiadiazolines are associated with the sp^3-hybridised 5-carbon atom and its methine proton. The 5-carbon resonates in the ^{13}C n.m.r. spectrum of (2a) at δ 70.5, the signal appearing as a doublet in the off-resonance spectrum. The methine proton resonates in the ^1H spectrum at δ 7.02, a position which betrays its strongly deshielded environment and which is far removed from the position (δ 8.3—9.0 p.p.m.) to be expected from an acyclic isomer such as (4), which would arise by straightforward imidoylation of thiourea. Nevertheless, it should be noted that both these features are also compatible with the discarded dihydrothiatriazepine formulation (3). Rejection of (3) in favour of (2a) is more difficult spectroscopically, but follows from (*i*) examination of the tautomerism in the 4-amidine unit, discussed below; and (*ii*) comparison with the spectroscopic properties of the 4-phenyl analogue (5). This was prepared by the method of Wuyts [4] and shown to display very similar spectroscopic features, in particular the 5-methine proton resonance at δ 6.83 and the 5-carbon resonance at δ 73.2.

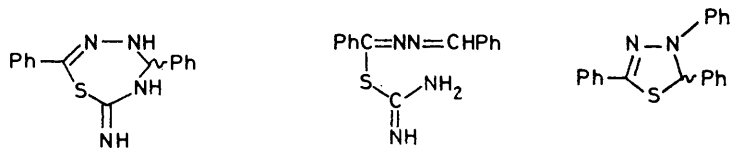
Two other 4-amidino-Δ^2-thiadiazolines have so far been prepared from thiourea, namely the 2-(4-chlorophenyl) and 2-(4-methoxyphenyl) analogues (2b) and (2c). All three amidines are strongly basic, forming hydrobromides or hydrochlorides which are stable in the

corresponding concentrated acid even at 100 °C; in the case of (2a) a stable acetate salt, m.p. 185—187 °C, was also isolated after an attempt to acetylate it using glacial acetic acid. These three bases all display the characteristic reactivity of amidines, namely susceptibility to



(1) (2)

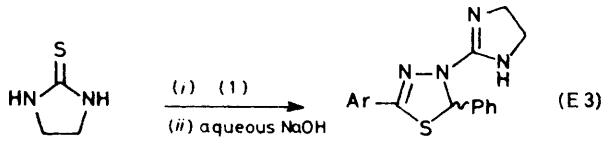
a; Ar = Ph; b; Ar = 4-ClC_6H_4; c; Ar = 4-$MeOC_6H_4$.



(3) (4) (5)

alkaline hydrolysis under forcing conditions and participation in cyclo-condensations when treated with 1,3-dicarbonyl compounds.[11]

Reaction of Imidazolidine-2-thione with Chlorodiazabutadienes.—The cyclic thiourea imidazolidine-2-thione (ethylenethiourea) also reacts rapidly with the 1-chlorodiphenyldiazabutadiene (1a) at ambient temperature. The product, a hydrochloride, is converted into the corresponding free base (6a) with aqueous alkali in 74% overall yield [equation (E3)].

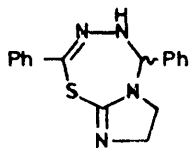


(6)

a; Ar = Ph
b; Ar = 4-ClC_6H_4

The characteristic features of the 5-methine group (δ_C 71.2; δ_H 7.04) are also evident in the spectra of (6a). In addition, these spectra clearly display the features to be expected from a tautomeric 1,3-disubstituted amidine function, present in (6a) but not in the corresponding dihydrothiatriazepine isomer (7), which is thereby excluded. Moderately fast tautomerism results in the near degeneracy of both the ^{13}C and the ^1H n.m.r. signals for the two adjacent methylene groups in the cyclic amidine function. The effect of temperature on this portion of the continuous-wave ^1H n.m.r. spectrum of (6a) is particularly striking (Figure 1). Two *broad* ^{13}C n.m.r. signals were detected in the Fourier-transform spectrum of (6a); the effect of temperature on this ^{13}C spectrum has not yet been investigated. However, the ^{13}C spectrum of the analogous product (6b) was recorded not only in $CDCl_3$ (see Experimental section) but also in [$^2H_5$]pyridine at three temperatures in the range 258—373 K (Figure 2). At low temperature the imidazoline carbons are distinct, but at 373 K they appear as a single resonance (δ 49.9).

The conclusion inferred from these observations, that



(7)

a tautomeric amidine system is present, was reinforced by acetylation of (6a). This removes the residual NH proton responsible for the tautomerism, the effects of

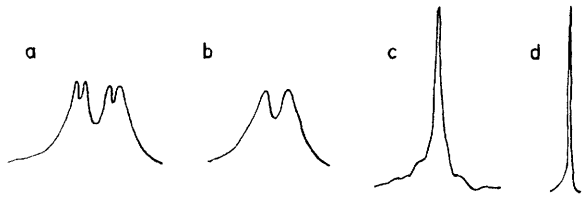


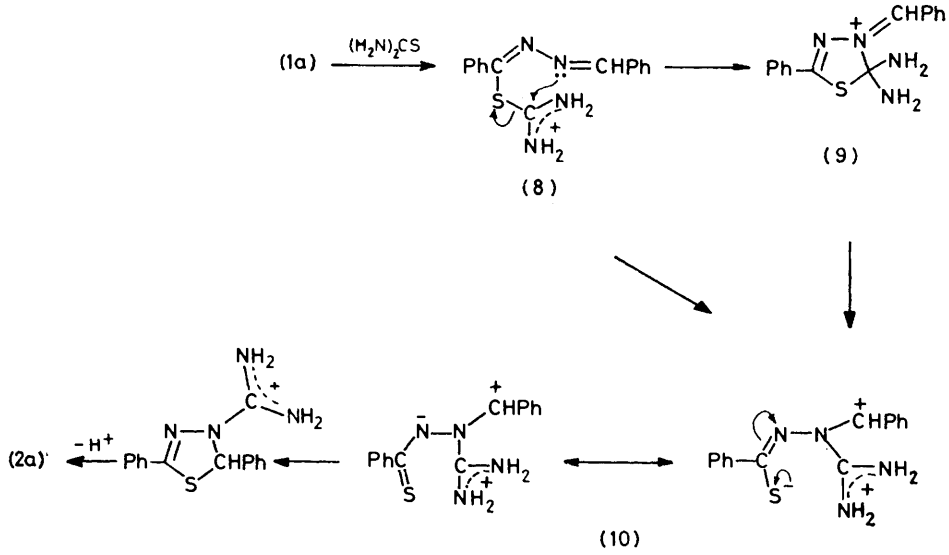
FIGURE 1 Temperature dependence of the CH_2–CH_2 portion of the ^1H n.m.r. spectrum of the Δ^2-thiadiazoline (6a) at 90 MHz: a In $CDCl_3$ at 223 K; b in $CDCl_3$ at 253 K; c in [$^2H_6$]dimethyl sulphoxide (DMSO) at 308 K; d in [$^2H_5$]DMSO at 373 K

which are no longer observable in the spectra of the acetyl derivative.[11]

The 2-(4-chlorophenyl)-Δ^2-thiadiazoline (6b) was obtained from the reaction of ethylenethiourea with the 1-(4-chlorophenyl)diazabutadiene (1b) and subsequent

basification. Its properties are generally similar to those of (6a), though as expected it and the monocyclic 4-chlorophenyl compound (2b) are more soluble in organic solvents than their non-chlorinated counterparts.

Mechanism of the Reaction.—It was first established that 1,4-diphenyldiazabutadiene (benzaldazine) is completely unreactive towards thiourea even after 100 h in refluxing ethanol. We therefore conclude that the initial step in the formation of the amidino-Δ^2-thiadiazolines (2) is nucleophilic replacement of chlorine in (1a) by thiourea, expected on the known behaviour of thiourea [12] to be initiated by the sulphur atom giving the diazabutadienylisothiouronium hydrochloride (8). This salt might have been expected to undergo facile 5-*exo*-trigonal [13] ring-closure on the basis of earlier studies of such diazabutadiene derivatives [8] and related hydrazones.[14] However, the incipient 5,5-diaminothiadiazoline (9) is either very unstable or never fully formed, because the product structure requires C–S cleavage at this point. Such a cleavage is well known to occur when thiuronium salts are subjected to nucleophilic attack by amines or hydrazines.[15] The resulting zwitterion (10) may be regarded as a 1,3- or a 1,5-dipole, from which the hydrochloride of (2a) arises by N–N bond rotation and ring-closure (Scheme 1). Electrocyclic rearrangements of 1,5-dipoles are well known and have recently been reviewed; [16] the mechanism proposed constitutes a further example of such rearrangements.



SCHEME 1

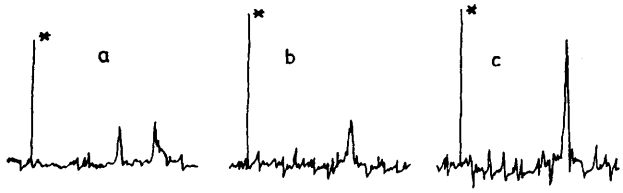
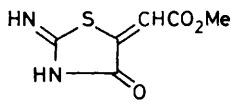


FIGURE 2 Temperature dependence of the CH_2–CH_2 portion of the ^{13}C n.m.r. spectrum of the Δ^2-thiadiazoline (6b) in [$^2H_5$]pyridine at 20.1 MHz: a 4 200 scans at 258 K; b 8 500 scans at 353 K; c 6 400 scans at 373 K (asterisked peak is *C*HPh at position 5 of the thiadiazoline ring)

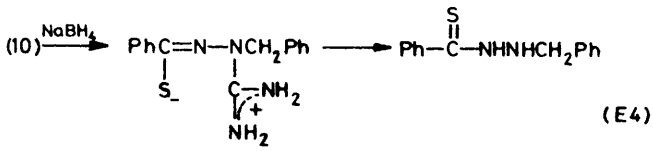
An analogy may be found in the formation of 2,5-disubstituted 1,3,4-oxadiaxoles by lead tetra-acetate oxidation of 1,4-diaryl-2,3-diazabutadienes.[17] Scheme 2 is adduced to explain this reaction and involves a very similar 5-*exo*-trigonal closure [13] followed by cleavage of the much stronger C–O bond.

Attempts to trap the dipolar intermediate (10) by conducting the reaction of (1a) with thiourea in the presence of added dipolarophiles have so far proved unsuccessful, most often owing to side-reactions such as the cycloaddition of thiourea to the dipolarophiles selected. Thus, tetracyanoethylene reacts rapidly with both thiourea and the chloride (1a) on their own, and no new products were formed when it was added to the reaction mixture leading to (2a). Dimethyl acetylenedicarboxylate was tried next, but the only product formed was identified as the known product of its reaction with thiourea, namely the iminothiazolidone (11).[18] Phenylacetylene was tested, on the basis of its lower reactivity, but again no trapped product resulted.



(11)

Limited success was achieved in a trapping experiment in which an excess of sodium borohydride, shown by control experiments not to reduce either of the reactants,



(E4)

(12)

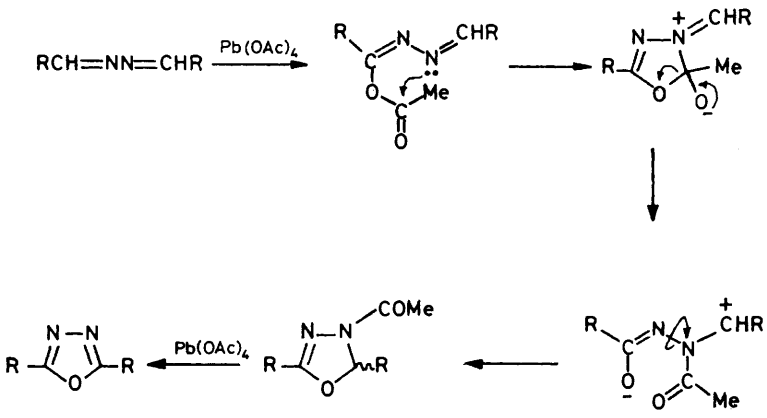
was present during the reaction of thiourea with (1a). Only one of the three detected products could be isolated: it was identified spectroscopically and by m.p. as the known N^2-benzylthiobenzoylhydrazine (12) (21%).[19] Its formation can be interpreted on the basis of reduction of the intermediate iminium ion (10), a type of reduction which borohydride has been reported to achieve[20] [equation (E4)].

EXPERIMENTAL

T.l.c. analyses were performed on Merck pre-coated sheets of silica gel 60 F_{254}. Flash chromatography[21] was performed on 55-mm or 35-mm outside diameter columns containing Merck silica gel 60, particle size 40—63 μm, usually monitored by t.l.c. Pure products were identified by i.r., using Perkin-Elmer models 197 and 397 diffraction grating spectrophotometers, u.v., using a Cary 118 X spectrophotometer, ^{1}H n.m.r., using Perkin-Elmer R12 (60 MHz) and R32 (90 MHz) and Varian HA 100 (100 MHz) spectrometers, ^{13}C n.m.r., recorded using a Brucker WP80 (20 MHz) or JEOL FX-60 (15 MHz) * spectrometer (all chemical shifts are cited relative to internal tetramethylsilane, positive values downfield), and mass spectrometry, using an A.E.I. MS902 or a Kratos MS45 spectrometer in conjunction with a Digital PDP 8/1 Data Acquisition Interface System.

The 1-chlorodiazabutadienes (1a—c) were prepared by treating the corresponding aroylhydrazones ArCONHN=CHPh with thionyl chloride as described previously.[8] Benzaldazine was prepared by the reaction of hydrazine hydrate with benzaldehyde.[22] Thiobenzoylthioglycolic acid (carboxymethyl dithiobenzoate), m.p. 120—122 °C (lit.,[23] m.p. 126—127 °C), was prepared in 42% yield from benzotrichloride by treatment with alkaline KHS followed by sodium chloroacetate.[24] N^2-Phenylthiobenzoylhydrazine (thiobenzhydrazide) was prepared (79%) by reaction of phenylhydrazine with thiobenzoylthioglycolic acid in aqueous alkaline solution,[25] and was purified by chromatography m.p. 76 °C (lit.,[5] m.p. 89—91 °C, but also noted [19] to be dimorphous with a low m.p. form, m.p. 69—70 °C).

Reactions of Thiourea.—(a) *With benzaldazine.* T.l.c. ($CHCl_3$) analysis showed no evidence of any reaction between thiourea (1.10 g, 14.4 mmol) and benzaldazine (3.0 g, 14.4 mmol) after 100 h in refluxing ethanol (anhydrous, 120 cm^3), and both reactants were recovered nearly quantitatively (100% and 97% respectively).



SCHEME 2

(b) *With 1-chloro-1,4-diphenyldiazabutadiene* (1a).[26] The 1-chlorodiphenyldiazabutadiene (1a) (24.3 g 100 mmol) was added in a single portion to a stirred suspension of thiourea (7.62 g, 100 mmol) in anhydrous ethanol (80 cm^3), and stirring was continued for 1 h. Diethyl ether (80 cm^3) was added, and the solid filtered and recrystallized from ethanol to give, after baking *in vacuo* at 110 °C for 6 h to remove ethanol of crystallization, *4-amidino-2,5-diphenyl-*Δ^2*-1,3,4-thiadiazoline hydrochloride* (26.6 g, 73 mmol, 73%) (Found: C, 56.2; H, 4.7; N, 17.9; S, 10.2; Cl, 11.2. $C_{15}H_{15}ClN_4S$ requires C, 56.5; H, 4.7; N, 17.6; S, 10.0; Cl, 11.1%), as white prisms, m.p. 175—179 °C; δ([$^2H_6$]dimethyl sulphoxide) 7.1—8.0 (m, Ar), and 8.39 (s, NH × 4). An aqueous solution of sodium hydroxide (3%, 900 cm^3) was rapidly added to a hot stirred solution of the hydrochloride (163 mmol) in ethanol (900 cm^3). The solution was allowed to cool and the precipitate was filtered off and washed with water, ethanol, and diethyl ether to give *4-amidino-2,5-diphenyl-*Δ^2*-1,3,4-thiadiazoline* (2a) (42.7 g, 151 mmol, 68% based on chlorodiazabutadiene) (Found: C, 63.6; H, 4.9; N, 19.9; S, 11.3%; M^+, 282. $C_{15}H_{14}N_4S$ requires C, 63.8; H, 5.0; N, 19.8; S, 11.6%; *M*, 282), m.p. 163—164 °C (dec.); δ_H (100 MHz) 4.50 ± 0.05 (s, 3 × NH), 7.02 (s, C*H*Ph), and 7.2—7.7 (2 × Ph); δ_C (15 MHz) 70.5 (d in off-resonance spectrum, *C*HPh), 125.3—130.3

* Courtesy of the Chemistry Department, University of York.

(Ar), 141.5 (C-1 of 5-Ph), 145.8 (C=N), and 154.5 (exocylic C=N); $\lambda_{max.}$ (EtOH) 318 (ε 9 100), 294 (7 000), and 256 nm (19 900); *m/e* (significant ions only) 282 (7%, *M*), 240 (67, *M* − H_2NCN), 239 (56), 179 (95, *M* − PhCN), 178 (35), 163 (91, *M* − PhCN − NH_2), 136 (22, *M* − PhCN − MeN_2), 135 (14, PhCNS), 121 (88, PhCS), 104 (100, PhCHN), 103 (34), 77 (81, Ph), and 43 (68, MeN_2).

(c) *With* 1-*chloro*-1-(4-*chlorophenyl*)-4-*phenyl*-2,3-*diazabutadiene* (1b). In the same way was prepared, *via* its hydrochloride, m.p. 137 °C [40%, from ethanol–light petroleum (b.p. 40—60 °C) (60 : 40)], 4-*amidino*-2-(4-*chlorophenyl*)-5-*phenyl*-Δ²-1,3,4-*thiadiazoline* (2b) (50% based on chlorodiazabutadiene) (Found: C, 56.6; H, 4.1; Cl, 11.1; N, 17.5; S, 10.1%; M^+, 316, 318. $C_{15}H_{13}ClN_4S$ requires C, 56.8; H, 4.2; Cl, 11.1; N, 17.7; S, 10.1%; *M*, 316), m.p. 164 °C [from light petroleum (b.p. 40—60 °C)]; δ_H (60 MHz) 4.62 (s, 3 × NH), 7.11 (s, C*H*Ph), 7.35 (s, Ph), and 7.47 (dd, 4-ClC_6H_4); δ_C (20 MHz) 70.8 (CHPh), 125.4—129.1 (Ar), 136.3 (C-1 of 5-Ph), 141.4 (C=N), and 144.7 (exocyclic C=N); $\lambda_{max.}$ (EtOH) 321 (ε 10 400), 297 (7 492), and 265 nm (23 300); *m/e* (significant ions and, where appropriate, ^{35}Cl components only are shown) 316 (1%, *M*), 274 (13, *M* − CH_2N_2), 197 (31, *M* − CH_2N_2 − Ph), 179 (31, *M* − ArCN), 161 (42, *M* − ArCS), 160 (44), 138 (22, ArCHN), 137 (52), 119 (34, $PhCH_2N_2$), 104 (63, PhCHN), 103 (23), 102 (29, *M* − ArCN − Ph), 84 (100, *M* − ArCS − Ph), 77 (67, Ph) and 43 (56, MeN_2).

(d) *With* 1-*chloro*-1-(4-*methoxyphenyl*)-4-*phenyl*-2,3-*diazabutadiene* (1c).[26] In the same way was prepared, *via* its hydrochloride, m.p. 153—154 °C (from EtOH); δ_H (100 MHz) ([$^2H_6$]dimethyl sulphoxide) 3.94 (s, MeO), 7.37 (s, C*H*Ph), 7.1—8.1 (dd, 4-$MeOC_6H_4$), 7.5 (s, Ph), and 8.35 (s, 4 × NH), 4-*amidino*-2-(4-*methoxyphenyl*)-5-*phenyl*-Δ²-1,3,4-*thiadiazoline* (2c) (61% based on the chlorodiazabutadiene) (Found: C, 61.1; H, 5.2; N, 17.9; S, 10.1%; M^+, 312. $C_{16}H_{16}N_4OS$ requires C, 61.5; H, 5.2; N, 17.9; S, 10.3%; *M*, 312), m.p. 173—174 °C; δ_H (100 MHz) ([$^2H_6$]dimethyl sulphoxide) 3.75 (s, MeO), 5.6 (3 × NH), 7.16 (s, C*H*Ph), 7.26 (s, Ph), and 6.8—7.8 p.p.m. (dd, 4-$MeOC_6H_4$).

(e) *With* 1-*chloro*-1,4-*diphenyldiazabutadiene in the presence of sodium borohydride*. 1-Chloro-1,4-diphenyl-2,3-diazabutadiene (2.0 g, 8.2 mmol) and then thiourea (628 mg, 8.2 mmol) were added to a stirred solution of sodium borohydride (930 mg, 25 mmol) in anhydrous ethanol (130 cm³) at room temperature; effervescence occurred. After 5 h, t.l.c. ($CHCl_3$) showed the absence of residual chlorodiazabutadiene and the presence of three components (R_F values 0.0, 0.25, and 0.40). The second component was isolated by evaporation, extraction with chloroform (100 cm³), washing of the chloroform solution with water (50 cm³), and evaporation of the dried chloroform layer *in vacuo*, leaving a residual oil to which diethyl ether was added (8 cm³). The precipitate was recrystallized from ethanol and identified spectroscopically as N^1-benzyl-N^2-(phenylthiocarbonyl)hydrazine (400 mg, 1.7 mmol, 20% based on diazabutadiene) (Found: C, 69.6; H, 5.8; N, 11.6; S, 13.0%; M^+, 242. Calc. for $C_{14}H_{14}N_2S$: C, 69.4; H, 5.8; N, 11.6; S, 13.2%; *M*, 242), m.p. 148—149 °C (lit.,[19] m.p. 147—148 °C); δ_H (60 MHz, $CDCl_3$) 7.80 (s, NH × 2), 7.75—7.20 (Ph × 2), and 4.14 (s, CH_2N); δ_C (20 MHz) 192.6 (C=S), 139.2—126.7 (Ar), and 54.3 p.p.m. (CH_2). It was shown in separate experiments that sodium borohydride does not react under these conditions with thiourea or with 4-amidino-2,5-diphenyl-Δ²-1,3,4-thiadiazoline, although a slow reaction does occur with the chlorodiphenyldiazabutadiene.

(f) *With* 1-*chloro*-1,4-*diphenyldiazabutadiene in the presence of dimethyl acetylenedicarboxylate*. Thiourea (630 mg, 8.3 mmol) was added to a stirred solution of 1-chloro-1,4-diphenyl-2,3-diazabutadiene (2.0 g, 8.2 mmol) and dimethyl acetylenedicarboxylate (9 mmol) in ethanol (110 cm³). A white solid was deposited; after 17 h it was collected and shown by m.p. and mixed m.p. (275 °C with decomp.) (lit.,[18] m.p. 275 °C) with an authentic sample to be 2-imino-5-methoxycarbonylmethylidene-4-thiazolidone (11) (1.51 g, 8.1 mmol, 98%). The authentic sample was prepared by treatment of thiourea with dimethyl acetylenedicarboxylate (83%).[18]

Reactions of 2-*Imidazolidinethione*.—(a) *With* 1-*chloro*-1,4-*diphenyl*-2,3-*diazabutadiene* (1a). The chloride (1a) (5.0 g, 20.6 mmol) was added to a stirred suspension of the thione (2.10 g, 10.6 mmol) in dry ethanol (50 cm³) at room temperature and the mixture was stirred for 1 h. Diethyl ether (50 cm³) was added and the solid was collected and recrystallized from methanol and identified as the *hydrochloride* of (6a) (5.8 g, 16.9 mmol, 82%) (Found: C, 58.9; H, 5.0; Cl, 10.7; N, 16.5; S, 9.3. $C_{17}H_{17}ClN_4S$ requires C, 59.2; H, 5.0; Cl, 10.3; N, 16.3; S, 9.3%), m.p. 301—302 °C (decomp.). An aqueous solution of sodium hydroxide (3%, 45 cm³) was added to a hot stirred solution of the hydrochloride (3.0 g, 8.7 mmol) in methanol (45 cm³), and the solution was allowed to cool. The solid which precipitated was collected and recrystallized from 50% aqueous ethanol to give 4-(4,5-*dihydroimidazolin*-2-*yl*)-2,5-*diphenyl*-Δ²-1,3,4-*thiadiazoline* (6a) (2.45 g, 7.9 mmol, 74% based on chlorodiazabutadiene) (Found: C, 66.0; H, 4.9; N, 18.2; S, 10.6%; M^+, 308. $C_{17}H_{16}N_4S$ requires C, 66.2; H, 5.2; N, 18.2; S, 10.4%; *M*, 308), m.p. 169—170 °C (decomp.); δ_H (100 MHz) 3.55 (s at 35 °C and above, CH_2CH_2), 4.7—4.9 (br s, NH), 7.04 (s, C*H*Ph), and 7.1—7.8 (m, 2 × Ph); δ_C (20 MHz) 45.2 (br s, $NHCH_2$), 53.5 (br s, $=NCH_2$), 71.2 (d in off-resonance spectrum, *C*HPh), 124.9—130.3 (2 × Ph), 141.4 (C-1 of 5-Ph), 146.4 (C=N), and 159.0 (imidazolinyl C=N), $\lambda_{max.}$ (EtOH) 329.0 (ε 7 600), 251.0 (15 000), and 221 nm (15 993); *m/e* (significant ions only) 308 (9%, *M*), 205 (95, *M* − PhCN), 204 (100, *M* − PhCHN), 172 (28, *M* − PhCHNS), 128 (70, *M* − PhCN − Ph), 121 (36, PhCS), 104 (34, PhCHN), 103 (37), 77 (36, Ph), and 69 (12, $C_3H_5N_2$).

(b) *With* 1-*chloro*-1-(4-*chlorophenyl*)-4-*phenyldiazabutadiene* (1b). In the same way was prepared, *via* its *hydrochloride* (67%) (Found: C, 53.8; H, 4.1; Cl, 18.7; N, 14.9; S, 8.6. $C_{17}H_{15}Cl_2N_4S$ requires C, 53.8; H, 4.2; Cl, 18.7; N, 14.8; S, 8.4%), m.p. 248 °C (from EtOH), 4-(4,5-*dihydroimidazolin*-2-*yl*)-2-(4-*chlorophenyl*)-5-*phenyl*-Δ²-1,3,-4-*thiadiazoline* (6b) (77% based on the hydrochloride) (Found: C, 59.8; H, 4.2; Cl, 10.4; N, 16.2; S, 9.4%; M^+, 342. $C_{17}H_{14}ClN_4S$ requires C, 59.6; H, 4.4; Cl, 10.3; N, 16.3; S, 9.3%; *M*, 342), m.p. 102—103 °C (EtOH); δ_H (60 MHz) 3.58 (br s, CH_2CH_2), 4.8 (br s, NH), 7.09 (s, C*H*Ph), 7.33 (s, Ph), and 7.45 (dd, 4-ClC_6H_4); δ_C (20 MHz) 45—55 (very br, CH_2CH_2 weakened by tautomerism of NH), 71.6 (*C*HPh), 125.6—128.8 (Ar), 136.1 (C-1 of 5-Ph), 141.2 (C=N), and 158.6 (imidazolinyl C=N); $\lambda_{max.}$ (EtOH) 334 (ε 10 200) and 260 nm (21 150); *m/e* (^{35}Cl components only) 342 (8%, *M*), 205 (100, *M* − ArCN), 204 (100), 172 (36, *M* − ArCHNS), 138 (17, ArCHN), 137 (36, ArCN), 128 (85, *M* − ArCN, −Ph), 121 (26, PhCS),

104 (27, PhCHN), 102 (17), 77 (21, Ph), and 69 (18, $C_3H_5N_2$).

Preparation of 2,4,5-*Triphenyl*-Δ^2-1,3,4-*thiadiazoline*.—Benzaldehyde (0.232 g, 9.4 mmol) was added to a stirred solution of N^2-phenylthiobenzoylhydrazine (1.0 g, 4.4 mmol), in ethanol (5 cm^3) followed by two drops of concentrated hydrochloric acid. The yellow precipitate was washed with aqueous potassium carbonate and recrystallized from methanol to give the readily oxidized 2,4,5-triphenyl-Δ^2-1,3,4-thiadiazoline (0.75 g, 62%) (Found: C, 75.9; H, 5.0; N, 8.9; S, 9.9. Calc. for $C_{20}H_{16}N_2S$: C, 76.0; H, 5.1; N, 9.3; S, 9.9%), m.p. 93 °C (lit.,[4] m.p. 97 °C); δ_H (60 MHz) 6.83 (s, C*H*Ph) and 7.16—7.8 (m, 3 × Ph); δ_C (20 MHz) 73.2 (*C*HPh) and 114.1—144.1 (3 × Ph and C=N); *m/e* (see ref. 27) 316 (*M*), 239, 207, 194, 180, 121, 105, 104, 91 (100%) and 77.

Reaction of 4-*Amidino*-2,5-*diphenyl*-Δ^2-1,3,4-*thiadiazoline* (2a) *with* HCl.—36% Hydrochloric acid (2 mmol HCl) was added to a refluxing solution of the 4-amidinodiphenyl-Δ^2-thiadiazoline (2a) (0.565 g, 2 mmol) in ethanol (20 cm^3), and the mixture was refluxed for 1 min. The solvent was removed *in vacuo* and the white crystalline residue recrystallized from ethanol (5 cm^3) and identified as the hydrochloride of (2a) (0.622 g, 1.98 mmol, 99% yield) by i.r. and n.m.r. comparison with the sample prepared from thiourea and the chlorodiazabutadiene, m.p. and mixed m.p. with authentic material 173 °C.

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