# Unsaturated Compounds containing Nitrogen. Part 5.[1] Reactions of 1,4-Dichloro-1,4-diphenyl-2,3-diazabutadiene with Nucleophiles

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1,4-Dichloro-1,4-diphenyl-2,3-diazabutadiene (1) reacts with potassium cyanate to give 5-phenyl-1,2,4-triazol-3(2*H*)-one (9), but with potassium thiocyanate it gives the 1-chloro-4-thiocyanato-2,3-diazabutadiene (3). The thiocyanate (3) is not isomerized by heat, but is hydrolysed by acid to a mixture of 2,5-diphenyl-1,3,4-oxadiazole and 2-amino-5-phenyl-1,3,4-thiadiazole. Sodium hydrosulphide, potassium ethylxanthate, and thiourea all convert the dichlorodiazabutadiene (1) into 2,5-diphenyl-1,3,4-thiadiazole, while 2-aminobenzenethiol converts it into 2-phenylbenzothiazole.

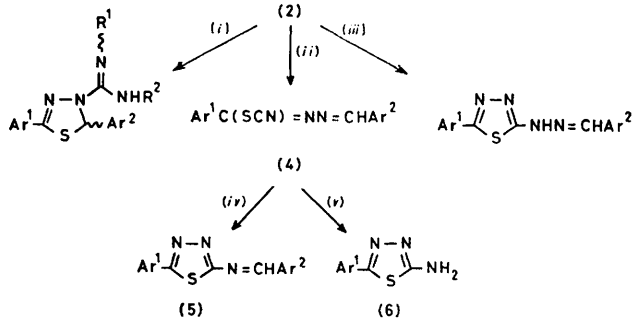


APART from an isolated physical-organic study of the mechanism of their solvolytic behaviour,[2] 1,4-dichloro-2,3-diazabutadienes such as (1) have received little attention since Stollé's early investigation of their synthesis and conversion into heterocyclic compounds.[3] We recently reported the attack by sulphur nucleophiles on the corresponding monochlorides (2) [1,4,5] leading to the synthesis of thiadiazoles and thiadiazolines (Scheme 1). This paper discloses the results of our investigation

PhCCl=NN=CClPh (1) Ar¹CCl=NN=CHAr² (2)

of some related reactions between the dichlorodiazabutadiene (1) and nucleophilic reagents.

*Reactions of* 1,4-*Dichloro*-1,4-*diphenyl*-2,3-*diazabutadiene* (1).—(a) *With potassium thiocyanate.* On treatment with an equimolar proportion of potassium thiocyanate in refluxing ethanol, the dichlorodiazabutadiene (1) was converted into a monosubstitution product (84%).




SCHEME 1 *Reagents: i*, $R^1NHCSNHR^2$, then base; *ii*, KSCN; *iii*, $H_2N{\cdot}CS{\cdot}NH{\cdot}NH_2$; *iv*, reflux in xylene; *v*, aqueous acid, then base.

This was an off-white solid, m.p. 101 °C, which displayed little tendency to react further to form a disubstitution product under these conditions. Its spectroscopic properties (*e.g.*, i.r. S–C≡N stretch at 2 165 $cm^{-1}$, absence of N=C=S stretch at 2 040—2 080 $cm^{-1}$) were incompatible with an isothiocyanate, and it was accordingly identified as the 1-chloro-4-thiocyanato-2,3-diazabutadiene (3) [equation (1)].

A t.l.c.-based comparison of the reactivities of (1) and (2; $Ar^1 = Ar^2 = Ph$) towards potassium thiocyanate showed that the dichloride (1) is much less reactive than the monochloride (2). This observation agrees with an earlier kinetic study of their relative solvolysis rates,[2]

$$PhCCl{=}NN{=}CClPh \xrightarrow[\text{reflux}]{KSCN,\ EtOH} PhC(SCN){=}NN{=}CClPh \quad (1)$$
(1) (3)

which indicated that the dichloride is approximately forty times less reactive than the monochloride.

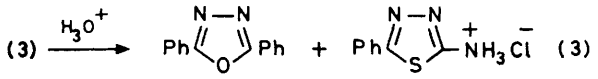
The reluctance of the chlorothiocyanatodiazabutadiene (3) to undergo further nucleophilic substitution by thiocyanate ion or by ethanol may be compared with the behaviour of the analogous chlorocyanide (7) which, although better prepared by a different route,[6] can be obtained by monosubstitution of the dichloride (1) by cyanide ion in a dipolar aprotic solvent.[7] The cyanide function does not completely inhibit further nucleophilic attack, however, since (7) reacts readily with secondary amines [as for example in equation (2)].[6]

$$(1) \xrightarrow{KCN} PhC(CN){=}NN{=}CClPh \xrightarrow{R_2NH} PhC(CN){=}NN{=}C(NR_2)Ph \quad (2)$$
(7)

Simultaneous displacement of both chlorine atoms in (1) by powerful nucleophiles such as azide or phosphide ions is also known.[8]

A further manifestation of the mutual interaction of the two functional groups in (3) became apparent when an attempt was made to cyclize (3) thermally. Unlike the thiocyanatodiazabutadienes (4), previously shown [1,4] to rearrange in refluxing xylene to thiadiazolyl Schiff's bases (5) (Scheme 1), the chlorothiocyanate (3) was stable under such conditions and could be recovered unchanged after 8 h. Although acid-catalysed cyclization of (3) does occur, the chlorothiocyanate being completely decomposed after 2 h in refluxing aqueous ethanolic hydrochloric acid, the product was mainly (61%) 2,5-diphenyl-1,3,4-oxadiazole (8) together with a low yield (17%) of the hydrochloride of (6; $Ar^1$ = Ph) [equation (3)]. In contrast, the thiocyanate (4; $Ar^1 = Ar^2$ = Ph) under the same conditions gave only the hydrochloride of the corresponding 2-aryl-5-amino-1,3,4-thiadiazole (6; $Ar^1$ = Ph) (Scheme 1).[1,4]

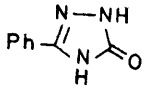
The mechanism by which (8) is formed, though not firmly established, must involve initial hydrolysis of either the chloride or thiocyanate function in (3). Base-catalysed cyclizations of chlorobenzalhydrazones, ArCCl=NNHCOR,[9] and ring closures of bis-hydrazines,



(8)

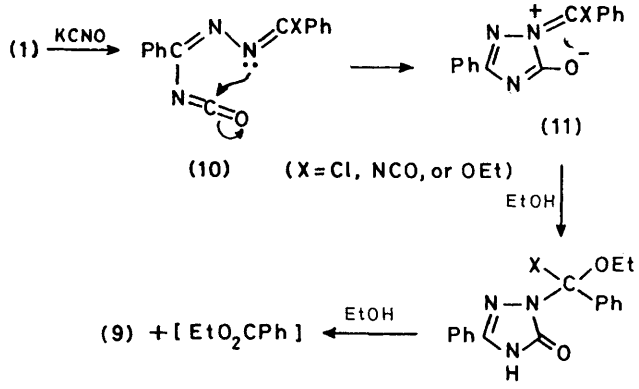
RCONHNHCOR, promoted by strong acid [10] are both known routes to 1,3,4-oxadiazoles. Either of these precursors could be formed by hydrolysis of (3).

(b) *With potassium cyanate.* The dichloride (1) reacted only sluggishly with potassium cyanate in refluxing ethanol and even after 20 h only 20% of the starting material was consumed. The principal product, isolated by sublimation from the residue which remained after leaching out unchanged starting material proved to be the known 5-phenyl-1,2,4-triazol-3(2*H*)-one [11] (9) (63%).



(9)

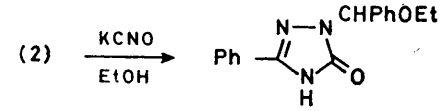
The formation of (9) demonstrates that at least one of the two chlorine atoms in (1) is replaced by cyanate, which attacks as usual *via* its nitrogen terminus rather than oxygen. We believe that the subsequent ring closure involves the addition to the cyanate π-system of the diazabutadiene nitrogen placed furthest from it. Such cyclizations are very common in the chemistry of functionalized diazabutadienes; they are best regarded as 5-*exo*-digonal and 5-*exo*-trigonal processes, using the terminology advocated by Baldwin.[12] The resulting zwitterionic intermediate (11) is then converted into the



Scheme 2

triazolone (9) by solvent ethanol, a pathway which should also lead to the formation of ethyl benzoate (Scheme 2).

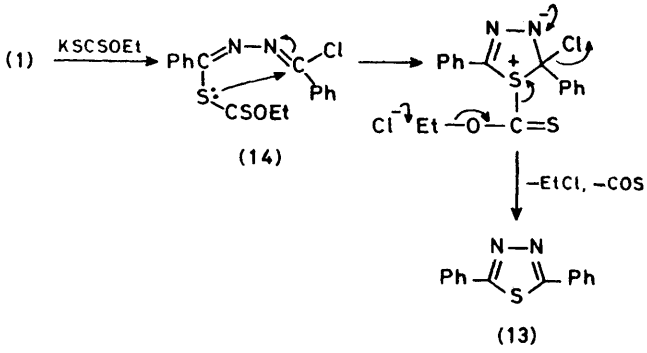
The recovery of a high proportion of unchanged starting material (1) suggests that the intermediates involved are (10) and (11) (where X = Cl), since replacement of the second chlorine in (1) is known to be more difficult than the first, and no monochlorocyanate (10; X = Cl) was detected. Support for this mechanism has been obtained in a previous investigation of the reaction of the monochloride (2; $Ar^1 = Ar^2 = Ph$) with potassium cyanate in ethanol, which yielded a triazolone (12) in which the trapping of the corresponding intermediate (11; X = H) by ethanol was evident.[13]



(12)

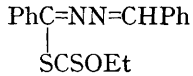
(c) *With potassium ethylxanthate.* The only product detected from several experiments in which various proportions of the dichloride (1) and the ethylxanthate (KSCSOEt) were kept in refluxing ethanol was 2,5-diphenyl-1,3,4-thiadiazole (13) (79%). No intermediate product could be detected (t.l.c.) during the early stages of the reaction.

The formation of the thiadiazole is attributed to intramolecular nucleophilic substitution by sulphur in the presumed monosubstitution product (14). The occurrence of such a fast 5-*endo*-trigonal cyclization, generally an unfavourable type of closure,[12] undoubtedly depends upon the size and powerful nucleophilicity of sulphur (Scheme 3). We recently reported [1] that the ethylxanthyldiazabutadiene (15) obtained from potassium



Scheme 3

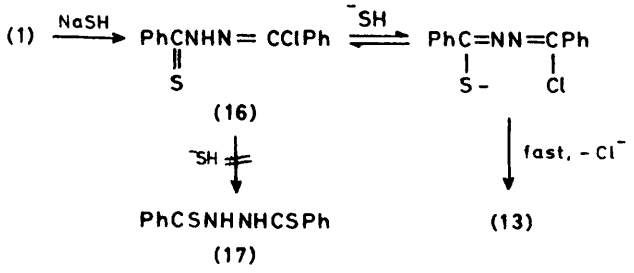
ethylxanthate and the monochloride (2; $Ar^1 = Ar^2 =$ Ph) was converted into the diphenylthiadiazole (13) on pyrolysis, the higher temperature in that instance being required because no satisfactory leaving group is available at the PhCH=N-terminus in (15), a role assumed by the second chlorine in the corresponding reaction of the dichloride (1).



(15)

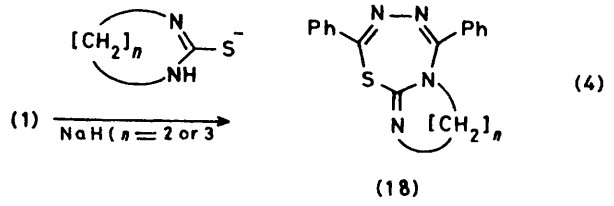
(d) *With sodium hydrosulphide.* In one of the early publications by Stollé on the properties of the dichloride

(1),[14] an unsuccessful attempt to convert the dichloride into diphenylthiadiazole (13) using hydrogen sulphide in an autoclave at 130 °C was reported. By contrast, we have observed that treatment of the dichloride (1) with sodium hydrosulphide in refluxing ethanol rapidly affords the thiadiazole (13) in excellent yield (84%). The facile cyclization under our conditions is attributable to the equilibrium between the thiohydrazide (16) obtained by monosubstitution and its conjugate anion, brought about by the presence of $SH^-$ ions. It seems improbable that a bis-thiohydrazide (17) is formed, since the reaction appeared to be completely unaffected by a two-fold increase in the sodium hydrosulphide concentration (Scheme 4).




SCHEME 4

(e) *With thiourea.* The formation of annelated thiatriazepines (18) by treatment of the dichloride (1) with anions of cyclic thioureas in the presence of an excess of sodium hydride was recently reported in a preliminary communication [15] [equation (4)]. That work was preceded by a prolonged study of the reactions of (1) with acyclic thioureas, full details of which will be reported separately.[16] Even in the absence of strong bases, thiourea and the dichloride react rapidly in refluxing ethanol, but the only product detected is the ubiquitous 2,5-diphenylthiadiazole (13) (75%).

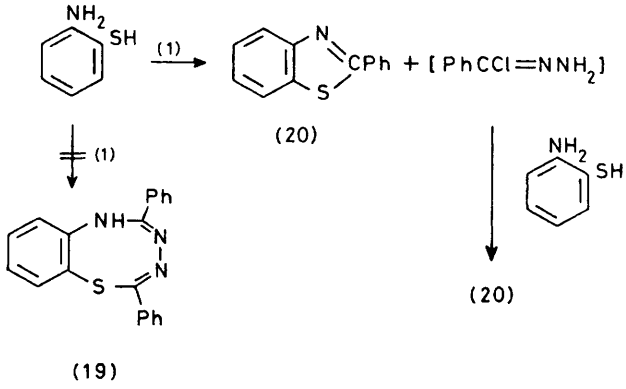



(4)

$$(1) \xrightarrow{H_2NCSNH_2} (13) + [H_2NCN] \text{ or } [HN{=}C{=}NH]_n$$

The residue of the thiourea must be eliminated as cyanamide or carbodi-imide, but no attempt was made to isolate them or any products of their reaction with the solvent.

(f) *With 2-aminobenzenethiol.* A fast reaction occurred when the dichloride (1) was gently refluxed with a large excess of 2-aminobenzenethiol in ethanol, a reaction from which it was hoped that the novel heterocyclic system (19) might be obtained. On cooling the solution, a product precipitated which was identified as the well known 2-phenylbenzothiazole (20), a product previously obtained by similar treatment of the monochloride (2; $Ar^1 = Ar^2 = Ph$).[1] The optimum yield (67%), achieved by taking a greater-than-fourfold excess of 2-aminobenzenethiol, indicated that both of the imidoyl chloride




SCHEME 5

units of the dichlorodiazabutadiene (1) had participated, which suggested the sequence shown in Scheme 5.

## EXPERIMENTAL

Chromatographic and spectroscopic techniques employed have been described previously.[1] Technical potassium thiocyanate was purified by recrystallization from 30% aqueous ethanol and was stored over $P_2O_5$. Sodium hydrosulphide was prepared by passing $P_2O_5$-dried hydrogen sulphide into a solution of sodium ethoxide in dry ethanol at 60 °C, and was precipitated by the addition of a large excess of anhydrous ether; yield 85%, m.p. 347—348 °C (lit.,[17] 350 °C). 1,4-Dichloro-1,4-diphenyldiazabutadiene was prepared by slow chlorination of benzaldazine [18] in glacial acetic acid solution at room temperature; yield 73%, m.p. 121—122 °C (from ethanol) (lit.,[19] 123 °C).

*Reactions of* 1,4-*Dichloro*-1,4-*diphenyl*-2,3-*diazabutadiene* (1).—(a) *With potassium thiocyanate.* The dichlorodiphenyldiazabutadiene (1) (2.32 g, 8.3 mmol) and potassium thiocyanate (0.81 g, 8.4 mmol) were kept in gently refluxing dry ethanol (50 $cm^3$) for 75 min, and the hot solution was filtered to remove potassium chloride. The filtrate was kept at −25 °C, and deposited a solid which was recrystallized from ethanol and identified as 1-*chloro*-1,4-*diphenyl*-4-*thiocyanato*-2,3-*diazabutadiene* (3) (2.1 g, 84%) (Found: C, 60.0; H, 3.4; N, 13.9; S, 11.1; Cl, 11.5%; $M^+$, 299. $C_{15}H_{10}ClN_3S$ requires C, 60.1; H, 3.4; N, 14.0; S, 10.7; Cl, 11.8%; *M*, 299), m.p. 101 °C, $\nu_{max.}$ 3 080w, 2 940w, 2 175w, 2 165w, 1 610m, 1 597m, 1 578m, 1 495w, 1 455m, 1 320w, 1 226m, 1 210m, 1 184m, 1 155w, 1 080w, 1 035w, 1 000m, 946m, 934m, 921s, 912m, 905w, 847m, 772w, 700m, 690m, and 682s $cm^{-1}$, δ($CDCl_3$) 7.2—8.3 (Ph).

(b) *With potassium cyanate.* The dichloride (1) (6.94 g, 25 mmol) and potassium cyanate (2.03 g, 25 mmol) were kept in refluxing ethanol (250 $cm^3$) for 21 h. The solution was filtered hot, the filtrate evaporated almost to dryness *in vacuo*, and the resulting precipitate was extracted with chloroform (50 $cm^3$) to remove unchanged starting material. The residue was sublimed *in vacuo* at 160 °C to give 5-phenyl-1,2,4-triazol-3(2*H*)-one (9) (0.4 g, 63% based on dichloride consumed) (Found: C, 59.6; H, 4.7; N, 26.4%; $M^+$, 161. Calc. for $C_8H_7N_3O$: C, 59.6; H, 4.4; N, 26.1%; *M*, 161), m.p. 322 °C (lit.,[11] 322 °C), δ([$^2H_6$]DMSO) 12.0 (s,

NH), 11.6 (s, NH), and 7.2—8.0 (m, Ph). Unchanged dichlorodiazabutadiene (1) (5.9 g, 21 mmol) was recovered from the filtrate.

(c) *With potassium ethylxanthate.* The 1,4-dichlorodiazabutadiene (1) (2.51 g, 9.1 mmol) and potassium ethylxanthate (2.89 g, 18.1 mmol) were gently refluxed in dry ethanol (50 cm³) for 3.5 h and the solution was immediately filtered and then evaporated *in vacuo* to *ca.* 25 cm³. The concentrated solution was kept at −25 °C, and the precipitate which formed was collected and recrystallized. It was readily identified by comparison with authentic samples as 2,5-diphenyl-1,3,4-thiadiazole (13) (1.72 g, 79%) (Found: C, 70.4; H, 4.4; N, 11.5; S, 13.5%; $M^+$, 238. Calc. for $C_{14}H_{10}N_2S$: C, 70.6; H, 4.2; N, 11.7; S, 13.5%; *M*, 238), m.p. and mixed m.p. 141—142 °C (lit.,[20] 141—142 °C). In a second otherwise identical experiment using a 1 : 1 molar proportion of reactants, t.l.c. showed that only the diphenylthiadiazole and unchanged dichloride (1) were present.

(d) *With sodium hydrosulphide.* The dichloride (1) (3.0 g, 11 mmol) and sodium hydrosulphide (1.21 g, 22 mmol) were kept in refluxing ethanol (50 cm³) for 30 min and the hot solution was filtered, concentrated to half volume *in vacuo*, and then kept at −25 °C. The white precipitate which resulted was collected and identified as 2,5-diphenylthiadiazole (13) (2.2 g, 84%), m.p. and mixed m.p. with authentic material 141—142 °C. In a separate experiment using an equimolar proportion of reagents, no other product than the thiadiazole was detected.

(e) *With thiourea.* The dichloride (1) (3.02 g, 11 mmol) and thiourea (0.82 g, 11 mmol) were refluxed in dry ethanol (50 cm³) for 4 h, and the solution was then concentrated to half volume and cooled to −25 °C. The resulting precipitate was identified as the diphenylthiadiazole (13) (1.93 g, 74%) as above; it was the only product detected.

(f) *With 2-aminobenzenethiol.* The 1,4-dichlorodiazabutadiene (1) (1.0 g, 3.6 mmol) and 2-aminobenzenethiol (2.25 g, 18 mmol) were kept in refluxing dry ethanol (20 cm³) for 1 h, when t.l.c. showed that no residual dichloride was present. The solution was concentrated and chilled, and the resulting precipitate identified as 2-phenylbenzothiazole (20) (1.02 g, 67% based on available phenyl groups), m.p. and mixed m.p. with an authentic sample [1] 115 °C.

*Attempted Thermal Isomerization of 1-Chloro-1,4-diphenyl-4-thiocyanato-2,3-diazabutadiene.*—Solutions of the chlorothiocyanate (3) (0.3 g) in (*a*) anhydrous xylene (10 cm³) and (*b*) anhydrous benzene (10 cm³) were heated under reflux (8 h); t.l.c. ($CHCl_3$) then showed only unchanged starting material.

*Hydrolysis of 1-Chloro-1,4-diphenyl-4-thiocyanato-2,3-diazabutadiene* (3).—The thiocyanate (3) (4.2 g, 14 mmol) was dissolved in ethanol (40 cm³) and the solution treated with 20 cm³ 2M-hydrochloric acid and then heated under reflux (2 h). T.l.c. showed three components, one of which was identified as benzoic acid. The solution was evaporated to dryness *in vacuo*, the residue extracted with boiling water (25 cm³), and the solid which remained was recrystallized from aqueous ethanol and identified as 2,5-diphenyl-1,3,4-oxadiazole (8) (1.9 g, 61%) (Found: $M^+$, 222. Calc. for $C_{14}H_{10}N_2O$: *M*, 222), m.p. 137 °C (lit.,[21] 138 °C). The aqueous extract was concentrated, cooled, and the resulting precipitate recrystallized from water and identified as the hydrochloride of 2-amino-5-phenyl-1,3,4-thiadiazole (6; $Ar^1$ = Ph) (0.5 g, 17%), m.p. and mixed m.p. with authentic material 213—214 °C (lit.,[22] 213—214 °C). An authentic sample of 2-amino-5-phenyl-1,3,4-thiadiazole hydrochloride was prepared (61%) by oxidation of benzaldehyde thiosemicarbazone at 90 °C with aqueous ferric chloride.

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