Unsaturated Compounds containing Nitrogen. Part 4.[1] Further Reactions of 1-Chloro-2,3-diazabutadienes with *S*-Nucleophiles

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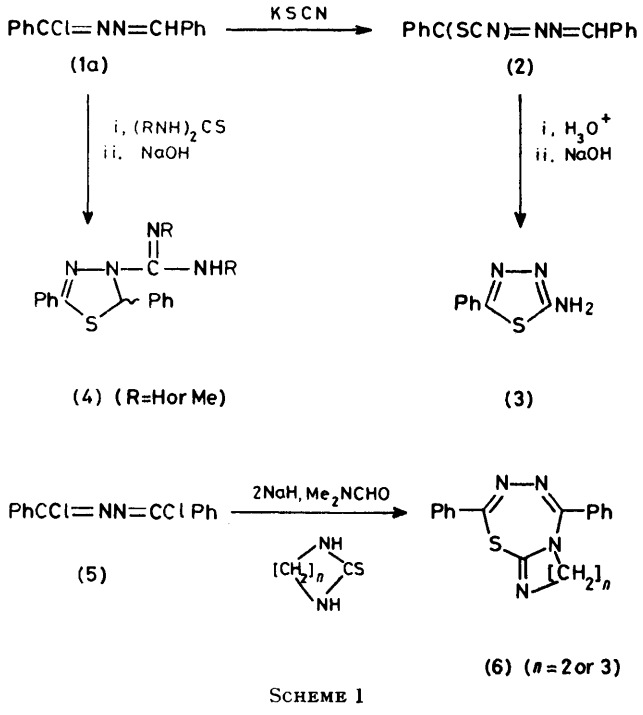
1-Chloro-1,4-diaryl-2,3-diazabutadienes ($Ar^1CCl{=}NN{=}CHAr^2$), prepared by the reaction of thionyl chloride with aroylhydrazones ($Ar^1CONHN{=}CHAr^2$), react with thiosemicarbazide or thiocarbohydrazide to give 2-arylidenehydrazino-5-aryl-1,3,4-thiadiazoles, and with potassium thiocyanate to give 1-thiocyanato-1,4-diaryl-2,3-diazabutadienes which isomerize thermally to arylideneamino-5-aryl-1,3,4-thiadiazoles. 1-Chloro-1,4-diphenyl-2,3-diazabutadiene reacts with potassium ethylxanthate to give a 1-ethylxanthyl-2,3-diazabutadiene which on pyrolysis yields 2,5-diphenyl-1,3,4-thiadiazole.

In this series we report the results of an investigation into the utility of 1-mono- and 1,4-di-substituted 2,3-diazabutadienes (–CX=NN=C< and –CX=NN=CY–) as intermediates in heterocyclic synthesis. Thus, we have previously shown that 1-chloro-1,4-diphenyl-2,3-diazabutadiene (1a) reacts with potassium thiocyanate to give the thiocyanato-2,3-diazabutadiene (2), which proved to be a useful synthon for 2-amino-1,3,4-thiadiazole (3) as a result of its facile acid-catalysed cyclization.[2] Similarly, the chlorodiazabutadiene (1a) has been found to



Scheme 1

react readily with thioureas to give 4-amidino-Δ^2-1,3,4-thiadiazolines (4),[1] while the analogous 1,4-dichloro-1,4-diphenyl-2,3-diazabutadiene (5) is converted by the anions of cyclic thioureas into annelated 1,3,4,6-thiatriazepines (6) [3] (Scheme 1).

Any further exploitation of these synthetic pathways will depend, however, upon the availability of chlorodiazabutadienes bearing a variety of 1,4-residues. We have accordingly tested the scope of the method reported previously for their preparation, namely, the reaction of thionyl chloride with aroylhydrazones;[4] in particular, we have attempted to extend this technique to the synthesis of chlorodiazabutadienes in which either or both of the 1- and 4-residues are alkyl groups. A new reaction between 1-chloro-2,3-diazabutadienes and thiosemicarbazide has been studied and found to provide a useful alternative to existing routes to thiadiazolylhydrazines. Further examples of the reaction of 1-chloro-2,3-diazabutadienes with potassium thiocyanate, and the thermal rearrangement of the 1-thiocycanatodiazabutadienes produced, have also been investigated.

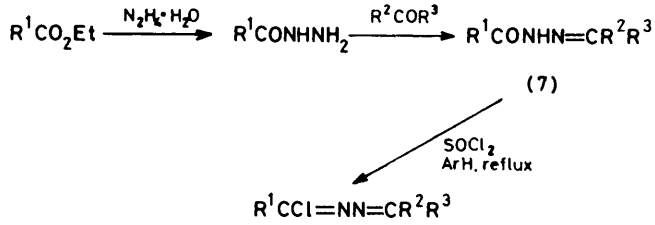
Reaction of Thionyl Chloride with Aroylhydrazones.—When the hydrazone (7) is one derived from an aromatic ester and an aromatic aldehyde (*i.e.*, R^3 = H, R^1 and R^2 both aryl) the method represented by Scheme 2 has few limitations. Provided the aryl groups contain no functions reactive towards thionyl chloride, yields are generally excellent (80—100%); a further ten 1-chloro-1,4-diaryl-2,3-diazabutadienes (1b—k) have now been prepared in this way, in addition to those reported previously.[4] Yields are reduced significantly in cases such as (1e), in which a strongly electron-releasing group is attached to one of the phenyl groups: for example, the symmetrical aldazine $(4\text{-}MeOC_6H_4CH{=}N)_2$ was detected (20%) during the preparation of (1e), although the formation of this by-product can be controlled to some extent by performing the chlorination and subsequent extraction at the lowest practicable temperature (*ca.* 60 °C).

The use of a more polar solvent, such as acetonitrile, in place of the usual toluene, or the addition of a small proportion of a tertiary base such as pyridine, are effective means of accelerating the chlorination. This is consistent with a mechanism which involves the rate determining decomposition of an intermediate chlorosulphite (8).[5] In the absence of these modifications,

$R^1C(OSOCl){=}NN{=}CHR^2$
(8)

chlorination is slow with 4-nitrophenylhydrazones such as (7; R^3 = H, R^1 = Ph, R^2 = $4\text{-}NO_2C_6H_4$) and with 3- and 4-pyridylhydrazones (7; R^3 = H, R^1 = Ph, R^2 =

3- or 4-pyridyl, and R^1 = 3- or 4-pyridyl, R^2 = Ph). In the case of the pyridylhydrazones, the hydrochlorides of the corresponding chloro-2,3-diazabutadienes were isolated, displaying broad N–H stretching i.r. bands at 2 300—2 410 cm^{-1} and strongly deshielded aromatic ^1H n.m.r. resonances (δ up to 9.7). No attempt was made to liberate the free bases from their hydrochlorides, owing to the reactivity of the imidoyl chloride function.

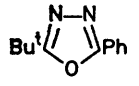


(1)

a; R^1 = Ph, R^2 = H, R^3 = Ph
b; R^1 = Ph, R^2 = H, R^3 = 4-MeC_6H_4
c; R^1 = Ph, R^2 = H, R^3 = 4-ClC_6H_4
d; R^1 = Ph, R^2 = H, R^3 = 4-BrC_6H_4
e; R^1 = Ph, R^2 = H, R^3 = 4-$MeOC_6H_4$
f; R^1 = 4-MeC_6H_4, R^2 = H, R^3 = Ph
g; R^1 = 3-MeC_6H_4, R^2 = H, R^3 = Ph
h; R^1 = 2-MeC_6H_4, R^2 = H, R^3 = Ph
i; R^1 = 4-ClC_6H_4, R^2 = H, R^3 = Ph
j; R^1 = 4-$MeOC_6H_4$, R^2 = H, R^3 = Ph
k; R^1 = 4-ClC_6H_4, R^2 = H, R^3 = 4-MeC_6H_4
l; R^1 = t-Bu, R^2 = H, R^3 = Ph
m; R^1 = t-Bu, R^2 = H, R^3 = 4-MeC_6H_4
n; R^1 = t-Bu, R^2 = H, R^3 = 4-ClC_6H_4
o; R^1 = t-Bu, R^2 = H, R^3 = 4-$NO_2C_6H_4$
p; R^1 = Me_2CH, R^2 = H, R^3 = Ph
q; R^1 = Me_2CH, R^2 = H, R^3 = 4-ClC_6H_4

SCHEME 2

Reactions between thionyl chloride and those aroylhydrazones (7; R^1 = Ph, R^2 = H, R^3 = Me, MeCH=CH, PhCH=CH, or H; R^1 = Ph, R^2 = R^3 = Me; and R^1 = Ph, R^2R^3 = $[CH_2]_n$, where n = 4 or 5) derived from aliphatic or αβ-unsaturated aldehydes, or from aliphatic or alicyclic ketones, invariably gave tarry products from which only benzoyl chloride was isolated. Occasionally such reactions lead to cyclization: thus, the hydrazone (7; R^1 = Ph, R^2 = H, R^3 = Bu^t) gave, after distillation of the initial product mixture, an oil shown by ^1H n.m.r. to consist of a mixture of two components, both of which contain a t-butyl group. G.c.–mass spectrometry enabled one of these to be identified as 5-phenyl-2-t-butyl-1,3,4-oxadiazole (9), but no eluant with a parent ion corresponding to the hoped-for chlorodiazabutadiene (1; R^1 = Ph, R^2 = H, R^3 = Bu^t) was detected.



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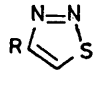
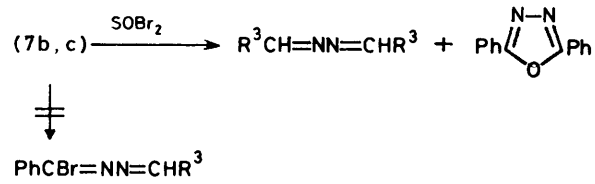


(10)

Since the treatment of hydrazones containing the $-CH_2C(Ar)=NNH-$ unit with thionyl chloride forms the basis of a known method for the synthesis of 1,2,3-thiadiazoles (10),[6] there is little scope for elaboration of the chlorodiazabutadiene synthesis in that direction. Indeed, we obtained only 4-(4-chlorophenyl)-1,2,3-thiadiazole (10; R = 4-ClC_6H_4) from a reaction between thionyl chloride and the benzoylhydrazone of 4-chloroacetophenone.

Reaction of Thionyl Chloride with Alkanoylhydrazones.—Cautious low-pressure distillation of the initial product mixtures generated by the treatment of pivaloyl- and isobutyryl-hydrazones (7; R^1 = Bu^t, R^2 = H, R^3 = Ph, 4-MeC_6H_4, 4-ClC_6H_4, or 4-$NO_2C_6H_4$) and (7; R^1 = Me_2CH, R^2 = H, R^3 = Ph or 4-ClC_6H_4) with thionyl chloride led to the isolation of rather unstable 1-alkyl-1-chloro-4-aryl-2,3-diazabutadienes (1l—q). These were not studied further, since they appeared to decompose on standing under nitrogen at room temperature. No 1-alkyl-1-chlorodiazabutadienes were isolated from reactions between hydrazones containing the CH_2-CONHN< unit [*e.g.*, (7; R^1 = Me, Et, or $PhCH_2$, R^2 = H, R^3 = Ph)] and thionyl chloride, and extensive decomposition was indicated by the isolation of benzonitrile and benzal chloride.

Reaction of Thionyl Bromide with Aroylhydrazones.—An unsuccessful attempt was made to prepare 1-bromo-1,4-diaryl-2,3-diazabutadienes (11) by the treatment of aroylhydrazones of aromatic aldehydes with thionyl bromide. Several examples were examined, but the only products which could be isolated and identified were symmetrical aldazines and 2,5-diaryl-1,3,4-oxadiazoles.



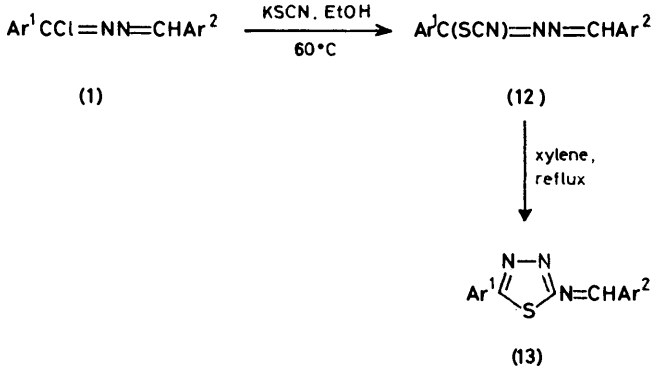
(11)

Reaction of 1-Chloro-2,3-diazabutadienes with Potassium Thiocyanate.—The previously reported reaction [2] between 1-chloro-2,3-diazabutadiene (1a) and potassium thiocyanate has been shown to be of general application. Seven new thiocyanatodiazabutadienes (12b—h) have been synthesized in yields varying from 60 to 85%. They are all yellow solids, their ^1H n.m.r. spectra confirming the presence of an aldehyde-like proton (δ 8.5—8.7). In none of these reactions was the formation of an isothiocyanate detected (Scheme 3).

When either of the aromatic groups in (1) is a 4-nitrophenyl group, only polymeric gums are formed and none of the desired thiocyanate can be isolated, even after prolonged reaction times. This suggests that the S_N1 mechanism proposed [5] for replacement of chlorine in 1-chloro-1,4-diaryl-2,3-diazabutadienes in neutral or dilute alkaline solutions also holds for substitution by thiocyanate ion. No marked steric hindrance was observed when an *ortho*-methyl substituent was present in the aromatic group next to the site of substitution,

although the yield of the thiocyanate (12 g) was slightly reduced (60%).

The new thiocyanates (12b—g) were found to be readily converted on heating in xylene solution into the corresponding Schiff's bases (13b—g) of 5-amino-2-aryl-1,3,4-thiadiazoles (Scheme 3). The relatively low

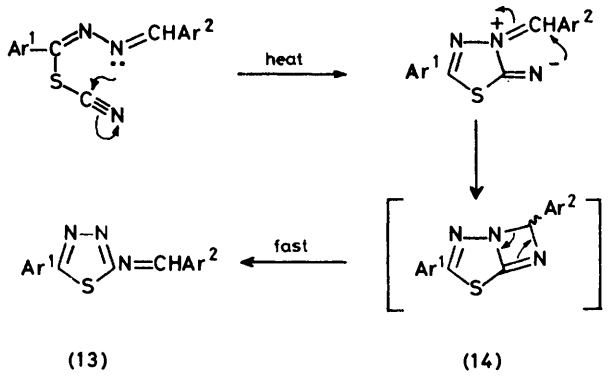


a; $Ar^1 = Ar^2 = Ph$
b; $Ar^1 = Ph$, $Ar^2 = 4\text{-}MeC_6H_4$
c; $Ar^1 = Ph$, $Ar^2 = 4\text{-}ClC_6H_4$
d; $Ar^1 = Ph$, $Ar^2 = 4\text{-}BrC_6H_4$
e; $Ar^1 = Ph$, $Ar^2 = 4\text{-}MeOC_6H_4$
f; $Ar^1 = 4\text{-}MeC_6H_4$, $Ar^2 = Ph$
g; $Ar^1 = 3\text{-}MeC_6H_4$, $Ar^2 = Ph$
h; $Ar^1 = 2\text{-}MeC_6H_4$, $Ar^2 = Ph$

SCHEME 3

yields (30—45%) are ascribed to the simultaneous formation of unidentified amorphous solid by-products, believed to be polymeric. The structures of the new arylideneaminothiadiazoles (13b—g) were readily confirmed by the detection of an aldehyde-like proton in their ^1H n.m.r. spectra (δ 8.5—9.4) and by examination of their mass spectra, which display characteristic base peaks at m/e values corresponding to $(M - H^{\cdot})^+$.[2]

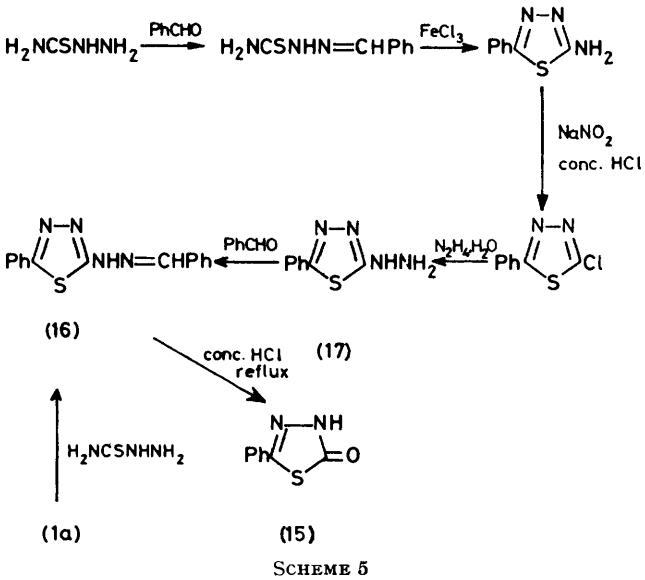
The mechanism proposed for the thermal isomerization of the thiocyanatodiazabutadienes (12) relies for the



SCHEME 4

transfer of the arylidene unit (Ar^2CH) on the formation of a bicyclic intermediate (14), presumed to undergo a rapid electrocyclic rearrangement (Scheme 4). Unfortunately, such an intermediate has so far not been detected by t.l.c. analysis of any of these reaction mixtures, even during the early stages of the reaction. It was argued that such an intermediate might be more readily detected if it were less highly strained. Accordingly, the reactions of 1-chlorodiazabutadienes (1) with thiosemicarbazide were investigated.

Reactions of Thiosemicarbazide with 1-Chlorodiazabutadienes (1).—The first 1-chloride investigated (1a) was found to react quite rapidly with thiosemicarbazide, and a solid product, $C_{14}H_{12}N_4S$, m.p. 248 °C, was readily isolated (66%). Its spectroscopic properties (*e.g.*, ^1H n.m.r. resonance at δ 8.1 p.p.m., C=N i.r. stretch at 1 610 cm^{-1}) suggested that, as in the thermal isomerization of the thiocyanatodiazabutadienes (12), a Schiff's base was formed. However, the substance initially resisted acid hydrolysis in ethanol, a reaction which normally cleaves the C=N bond in a Schiff's base. Only on digestion with concentrated hydrochloric acid was the supposed Schiff's base destroyed, the product then isolated being the known[7] 5-phenyl-1,3,4-thiadiazol-2(3*H*)-one (15) (62%). Several possible structures were considered for the supposed Schiff's base, including the benzylidenehydrazinothiadiazole (16); this compound



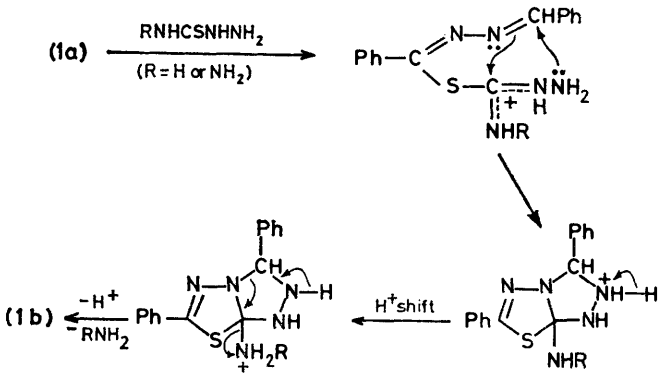
SCHEME 5

was previously prepared by a different route, when it was reported to have m.p. 256 °C.[8] This compound's precursor, the thiadiazolylhydrazine (17), was therefore synthesized according to the sequence shown in Scheme 5 and was converted by condensation with benzaldehyde into the hydrazone (16). The sample of (16) prepared by this route was identical (i.r., n.m.r., and mixed m.p.) with the sample obtained by the reaction of thiosemicarbazide with the 1-chlorodiazabutadiene (1a) (Scheme 5).

The thiosemicarbazide–chlorodiazabutadiene reaction was found to be a general one for 1-chloro-1,4-diaryldiazabutadienes (1): four other thiadiazolylhydrazines [(16; $Ar^1 = Ph$, $Ar^2 = 4\text{-}MeC_6H_4$), (16; $Ar^1 = 4\text{-}ClC_6H_4$, $Ar^2 = Ph$ or $4\text{-}MeC_6H_4$), (16; $Ar^1 = 4\text{-}MeOC_6H_4$, $Ar^2 = Ph$)] were prepared in this way in

67—78% yield. Although no intermediate species was detected by t.l.c. in any of these reactions with thiosemicarbazide, a reaction mechanism can be proposed (Scheme 6) which is consistent with that advanced previously for the thiocyanate reaction.

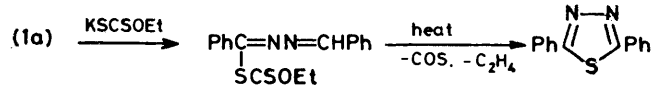
Reactions of 1-*Chloro*-1,4-*diphenyldiazabutadiene.*—(a) *With thiocarbohydrazide.* If the mechanism proposed in Scheme 6 for the reaction between thiosemicarbazide



SCHEME 6

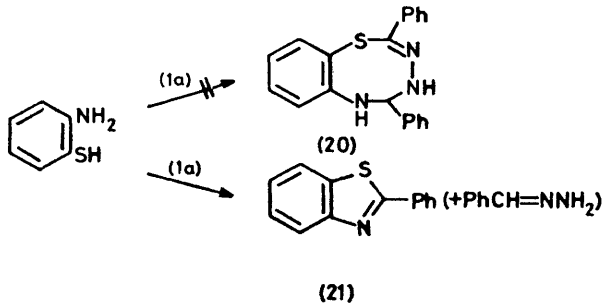
and 1-chlorodiazabutadienes such as (1a) is correct, replacement of thiosemicarbazide by the symmetrical thiocarbohydrazide in this reaction should also result in the formation of the thiadiazolylhydrazone (16). This deduction was put to the test by treating (1a) with thiocarbohydrazide, and upheld by the isolation of compound (16) (77%).

(b) *With potassium ethylxanthate.* The reaction between the chlorodiazabutadiene (1a) and potassium ethylxanthate has been reported by earlier workers [9] but without spectroscopic data for the proposed substitution product (18). The reaction was accordingly repeated, and the structure of (18) confirmed spectroscopically. It was of interest to determine the outcome of cyclization of (18), which might be expected to proceed by nucleophilic attack either by nitrogen upon the C=S bond, or by sulphur upon the C=N bond. The expected superiority of sulphur as a nucleophile was confirmed by the isolation of 2,5-diphenyl-1,3,4-thiadiazole (19) (69%) as the main product of the pyrolysis of (18).



(18) (19)

(c) *With* 2-*aminobenzenethiol.* To test whether it was possible to prepare larger heterocyclic ring systems from chlorodiazabutadienes, the chloride (1a) was treated with 2-aminobenzenethiol. It was hoped that such a 1,4-bis-nucleophile might convert the diazabutadiene into the eight-membered ring (20) but the only product isolated was the well known 2-phenylbenzothiazole (81%) (21). Such a reaction may be initiated by nucleophilic attack by sulphur, displacing chloride, and completed by elimination of benzaldehyde hydrazone, which was however not detected during the isolation of the benzothiazole.



(20) (21)

EXPERIMENTAL

I.r. spectra were obtained with a Perkin-Elmer 257 grating spectrophotometer, n.m.r. spectra with a Perkin-Elmer R10 or R20 spectrometer operating at 60 MHz, or a Varian HA-100 spectrometer operating at 100 MHz (δ values are positive downfield of internal Me_4Si unless stated otherwise), and mass spectra with an A.E.I. MS902 spectrometer with DS10 data acquisition. T.l.c. was performed on Eastman Chromatogram sheets precoated with 100 μm silica. The aroyl- and alkanoyl-hydrazines were prepared by the reaction of hydrazine hydrate with the corresponding ethyl esters; [10] yields were normally in excess of 70%. 2,2-Dimethylpropanoylhydrazine was prepared by azeotropic distillation of benzene–water from a vigorously refluxing mixture of 2,2-dimethylpropanoic acid, hydrazine hydrate, n-butanol, and benzene over activated alumina in a Dean-and-Stark apparatus, followed by distillation at reduced pressure, and was purified by recrystallization from light petroleum (b.p. 60—80 °C).

The aroyl- and alkanoyl-hydrazones were prepared by reaction of the corresponding aroyl- or alkanoyl-hydrazine with the appropriate aldehyde or ketone. The structures of those not previously reported were confirmed by spectroscopic analysis. Yields, m.p.s, and elemental analyses of hydrazones prepared are listed in Supplementary Publication No. SUP 22909 (13 pp.).* Technical potassium thiocyanate was purified by recrystallization from 30% aqueous ethanol and stored over P_2O_5. Thiocarbohydrazide was prepared (72%) by dropwise addition of carbon disulphide to cold hydrazine hydrate followed by an excess of water, and the resulting solution was heated at 90 °C (2 h), cooled, and the thiocarbohydrazide collected, m.p. 167—169 °C (lit.,[11] 169—170 °C). 2-Hydrazino-5-phenyl-1,3,4-thiadiazole, m.p. 184—185 °C (lit.,[12] 184—186 °C) was prepared (86%) by the reaction of an excess of hydrazine hydrate with 2-chloro-5-phenyl-1,3,4-thiadiazole, m.p. 83—84 °C (lit.,[12] 84.5 °C), itself obtained (77%) by diazotization of 2-amino-5-phenylthiadiazole in concentrated hydrochloric acid.

1-*Chloro*-1,4-*diaryldiazabutadienes* (1).—The chloroazines (1) were prepared by treatment of the appropriate aroylhydrazone with thionyl chloride in refluxing benzene or toluene, as described previously.[4] In those instances in which t.l.c. analysis showed incomplete reaction after 6 h, pyridine (0.1 cm^3) was added to accelerate the reaction.

* For details see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1979, Index issue.

Details of 1-chloroazines (1) prepared, including m.p.s, elemental analyses, and ^1H n.m.r. data, are given in SUP 22909. Also prepared by this method was 1-*chloro*-1,4,4-*triphenyl*-2,3-*diazabutadiene* (88%) (Found: C, 75.1; H, 5.0; N, 8.8; Cl, 11.1%; M^+, 318. $C_{20}H_{15}ClN_2$ requires C, 75.3; H, 4.7; N, 8.8; Cl, 11.1%; *M*, 318), m.p. 109—110 °C [from light petroleum (b.p. 60—80 °C)].

1-*Chloro*-4-(4-*methoxyphenyl*)-1-*phenyl*-2,3-*diazabutadiene* (1e). 1-Benzoyl-2-(4-methoxybenzylidene)hydrazine (5.84 g, 23 mmol), redistilled thionyl chloride (4.1 g, 34 mmol), and benzene (100 cm^3) were heated under reflux for 1 h, and the benzene and excess of thionyl chloride were removed *in vacuo*. The residue was first extracted with hot light petroleum (b.p. 40—60 °C) (200 cm^3) and the extract was concentrated to 20 cm^3 and kept at −25 °C for 12 h, yielding the *chloroazine* (1e) (3.6 g, 57%) (Found: C, 65.8; H, 4.9; N, 10.1; M^+, 272. $C_{15}H_{13}ClN_2O$ requires C, 66.0; H, 4.8; N, 10.3%; *M*, 272), m.p. 64—66 °C. Further re-extraction of the residue with hot petroleum (b.p. 100—120 °C) (100 cm^3) followed by hot ethanol, the combined extracts being kept at −25 °C for 12 h, gave, as a yellow solid, 1,4-bis-(4-methoxyphenyl)-2,3-diazabutadiene (1.2 g, 19%) (Found: C, 71.7; H, 6.2; N, 10.7%; M^+, 268. Calc. for $C_{16}H_{16}N_2O_2$: C, 71.6; H, 6.0; N, 10.4%; *M*, 268), m.p. 169—170 °C (lit.,[13] 169—170 °C) and benzoyl chloride.

1-*Chloro*-1-(4-*nitrophenyl*)-4-*phenyl*-2,3-*diazabutadiene*.—2-Benzylidene-1-(4-nitrobenzoyl)hydrazine (1.0 g, 3.7 mmol), redistilled thionyl chloride (1.6 g, 13 mmol), and benzene (50 cm^3) were heated under reflux for 84 h. The solution was evaporated almost to dryness, cooled, and filtered to afford the chlorodiazabutadiene (0.96 g, 90%) (Found: C, 58.4; H, 3.5; N, 14.6; Cl, 12.1%; M^+, 287. Calc. for $C_{14}H_{10}ClN_3O_2$: C, 58.4; H, 3.5; N, 14.6; Cl, 12.3%; *M*, 287), m.p. 135 °C (from EtOH) (lit.,[4] 135 °C). The above reaction was repeated with the addition of one drop of various organic bases and in different solvents; reactions were monitored by t.l.c. (benzene eluant). The times for complete disappearance of the benzylidenehydrazine are shown in the Table.

Effect of various catalysts on the rate of formation of 1-chloro-1-(4-nitrophenyl)-4-phenyl-2,3-diazabutadiene

Solvent	Catalyst	Reaction time/h
Benzene	None	34
Benzene	Pyridine	9.5
Benzene	Pyridine hydrochloride	9
Benzene	Dimethylformamide	8.5
Benzene	$PhNMe_2$	10
Benzene	Quinoline	9
Benzene	Hexamethylphosphoramide	8
Toluene	None	30
Acetonitrile	None	10
Acetonitrile	Pyridine	4

1-*Chloro*-1-*phenyl*-4-*pyridyl*- and 1-*Chloro*-4-*phenyl*-1-*pyridyl*-2,3-*diazabutadiene Hydrochlorides*.—In a typical experiment, 1-benzoyl-2-(3-pyridylmethylidene)hydrazine (2.75 g, 12 mmol) was dissolved in refluxing anhydrous toluene (50 cm^3) and redistilled thionyl chloride (4.36 g, 36.6 mmol) was added dropwise. Reflux was maintained for 12 h, and the solvent and thionyl chloride were then removed *in vacuo*. The residue was recrystallized from ethanol and identified as 1-*chloro*-1-*phenyl*-4-(3-*pyridyl*)-2,3-*diazabutadiene hydrochloride* (2.4 g, 70%) (Found: C, 55.5; H, 4.1; N, 14.8; Cl, 25.0. $C_{13}H_{11}Cl_2N_3$ requires C, 55.7; H, 4.0; N, 15.0; Cl, 25.3%), m.p. 198 °C (decomp.). Also prepared in this way were the isomeric 1-*chloro*-1-*phenyl*-4-(4-*pyridyl*)-2,3-*diazabutadiene hydrochloride* (75%) (Found: C, 55.1; H, 3.9; N, 15.1%), m.p. 187—190 °C (decomp.); 1-*chloro*-4-*phenyl*-1-(3-*pyridyl*)-2,3-*diazabutadiene hydrochloride* [76%, using xylene as solvent and refluxing (16 h)] (Found: C, 55.4; H, 4.0; N, 15.3; Cl, 25.6%), m.p. 176—178 °C (decomp.) [from light petroleum (b.p. 100—120 °C)–xylene]; and 1-*chloro*-4-*phenyl*-1-(4-*pyridyl*)-2,3-*diazabutadiene hydrochloride* (70%; using xylene solvent and 16 h reflux) (Found: C, 55.8; H, 4.13; N, 15.2; Cl, 25.3%), m.p. 200 °C (decomp.) [from xylene–light petroleum (b.p. 100—120 °C)]. ^1H N.m.r. data for these compounds are listed in SUP 22909.

1-*Chloro*-1-*alkyl*-4-*aryl*-2,3-*diazabutadienes*.—In a typical experiment, a mixture of 1-benzylidene-2-(2,2-dimethylpropanoyl)hydrazine (10.6 g, 52 mmol), redistilled thionyl chloride (9.25 g, 78 mmol), and dry benzene (100 cm^3) was heated under reflux for 1 h and the mixture was then evaporated *in vacuo* to give an oil. The oil was distilled (25 cm Vigreux) to give a pink oil identified as 1-*chloro*-1-(1,1-*dimethylethyl*)-4-*phenyl*-2,3-*diazabutadiene* (10.4 g, 90%) (Found: C, 65.2; H, 7.0; N, 12.3; Cl, 15.2. $C_{12}H_{15}ClN_2$ requires C, 64.7; H, 6.7; N, 12.6; Cl, 16.0%), b.p. 130 °C at 2 mmHg; δ (60 MHz; CCl_4) 6.9—7.9 (Ar), 7.89 (s, :CH), and 1.19 (s, Me_3C). Also prepared in this way were the following: 1-*chloro*-1-(1,1-*dimethylethyl*)-4-(4-*methylphenyl*)-2,3-*diazabutadiene* (80%) (Found: C, 66.2; H, 7.4; N, 11.7. $C_{13}H_{17}ClN_2$ requires C, 66.0; H, 7.2; N, 11.8; Cl, 15.0%), b.p. 143 °C at 3 mmHg, δ (60 MHz; neat) 7.59 (s, :CH), 6.4—7.4 (Ar), 1.78 (s, Me), and 0.92 (s, Me_3C); 1-*chloro*-4-(4-*chlorophenyl*)-1-(1,1-*dimethylethyl*)-2,3-*diazabutadiene* (80%) (Found: C, 56.4; H, 5.7; N, 10.6; Cl, 27.7. $C_{12}H_{14}Cl_2N_2$ requires C, 56.0; H, 5.5; N, 10.9; Cl, 27.6%), m.p. 59—60 °C [from light petroleum (b.p. 40—60 °C)], δ (60 MHz; CCl_4) 7.98 (s, :CH), 7.2—7.9 (Ar), and 1.33 (Me_3C); 1-*chloro*-1-(1,1-*dimethylethyl*)-4-(4-*nitrophenyl*)-2,3-*diazabutadiene* (83%) (Found: C, 54.2; H, 5.4; N, 15.4; Cl, 12.7. $C_{12}H_{14}ClN_3O$ requires C, 53.8; H, 5.2; N, 15.7; Cl, 13.2%), m.p. 110 °C [from light petroleum (b.p. 100—120 °C)], δ (100 MHz; $CDCl_3$) 8.08 (s, :CH), 7.8—8.4 (Ar), and 1.33 (s, Me_3C); 1-*chloro*-1-(1-*methylethyl*)-4-*phenyl*-2,3-*diazabutadiene* (86%) (Found: C, 63.3; H, 6.3; N, 13.3; Cl, 17.5%; M^+, 208. $C_{11}H_{13}ClN_2$ requires C, 63.3; H, 6.3; N, 13.4; Cl, 17.0%; *M*, 208), b.p. 120 °C at 3 mmHg, δ (60 MHz; CCl_4) 7.95 (s, :CH), 7.0—7.9 (Ar), 2.78 (septet, $CHMe_2$), and 1.13 (d, Me_2CH); and 1-*chloro*-4-(4-*chlorophenyl*)-1-(1-*methylethyl*)-2,3-*diazabutadiene* (85%) (Found: C, 53.7; H, 4.9; N, 11.0; Cl, 30.6%; M^+, 242. $C_{11}H_{12}Cl_2N_2$ requires C, 54.3; H, 5.0; N, 11.5; Cl, 29.2%; *M*, 242), b.p. 152 °C at 2 mmHg, δ (60 MHz, CCl_4) 7.9 (s, :CH), 6.9—7.7 (Ar), 2.71 (m, $CHMe_2$), and 1.16 (d, Me_2CH). Extreme care was needed to avoid decomposition during distillation and storage of the last two compounds, which readily decomposed to black tars. An 85 : 15 mixture (2.5 g) of benzal chloride and benzonitrile was the only identifiable material obtained from a similar reaction between thionyl chloride (5.0 g) and 1-acetyl-2-benzylidenehydrazine (4.5 g). When thionyl chloride was the solvent in this reaction, benzal chloride was mainly formed (contaminated with *ca.* 1% benzonitrile). 1-Propanoyl- and 1-phenylacetyl-2-benzylidenehydrazines behaved similarly.

Reactions of Thionyl Chloride.—(a) *With* 1-*benzoyl*-2-*alkylidenehydrazines*. In a typical reaction, 1-benzoyl-2-ethylidenehydrazine (5.0 g, 30 mmol), redistilled thionyl chloride (5.5 g, 46 mmol), and dry benzene (100 cm^3) were kept at reflux for 5 h, and solvent and the excess of thionyl

chloride were removed *in vacuo*. The residual oil was distilled at reduced pressure, but benzoyl chloride (2.5 g) and an unidentifiable dark tar were the only products. Similar results were obtained with the 1-benzoylhydrazines PhCONHN=CR^1R^2 (R^1 = H, R^2 = H, Me, CH=CHPh, or CH=CHMe, and where CR^1R^2 = cyclopentylidene and cyclohexylidene).

(b) *With 1-benzoyl-2-(α-methylbenzylidene)hydrazine.* The hydrazine (6.58 g, 27.6 mmol) and thionyl chloride (4.93 g, 41.4 mmol) were kept in refluxing benzene (100 cm^3) for 5 h. The solvent and excess of thionyl chloride were then removed, leaving a red oil from which a white solid separated. Low pressure distillation of the oil gave (i) a 4 : 1 mixture (0.8 g) of benzoyl chloride and acetophenone, and (ii) a further sample of the white solid (b.p. 90—100 °C at 1.5 mmHg) which was identified spectroscopically as 4-phenyl-1,2,3-thiadiazole (1.36 g, 30%) (Found: C, 58.9; H, 3.7; N, 17.1; S, 19.6%; M^+, 162. Calc. for $C_8H_6N_2S$: C, 59.3; H, 3.7; N, 17.3; S, 19.7%; *M*, 162), m.p. 77 °C [from light petroleum (b.p. 60—80 °C)] (lit.,[14] 77—79 °C).

(c) *With 1-benzoyl-2-(4-chloro-α-methylbenzylidene)hydrazine.* This gave 4-(4-chlorophenyl)-1,2,3-thiadiazole (35%) (Found: C, 48.3; H, 2.6; N, 14.5; S, 16.3; Cl, 18.2%; M^+, 196. Calc. for $C_8H_5ClN_2S$: C, 48.9; H, 2.6; N, 14.2; S, 16.3; Cl. 18.0%; *M*, 196), m.p. 137 °C (from EtOH) (lit.,[14] 137—139 °C).

(d) *With 2,5-diphenyl-3,4-diazahexa-2,4-diene.* The diazahexadiene (acetophenone azine) was prepared in 75% yield by heating a mixture of acetophenone (10 g), hydrazine hydrate (2.1 g), and 2M-hydrochloric acid (0.1 cm^3) in ethanol (50 cm^3) under reflux for 30 min.

Treatment of the diazahexadiene (2.4 g, 10 mmol) with thionyl chloride (1.2 g, 10 mmol) in refluxing benzene (50 cm^3) (3 h) gave a dark mixture which was evaporated and filtered. The resulting solid was recrystallised [light petroleum (b.p. 60—80 °C)] and then vacuum sublimed (60 °C at 2 mmHg) to afford 4-phenyl-1,2,3-thiadiazole (1.0 g, 62%), m.p. and mixed m.p. with an authentic sample 77 °C. The dark filtrate was distilled to give a 3 : 2 mixture of acetophenone and a component believed to be α-chlorostyrene, δ 5.04 and 5.24 ($^2J_{HH}$ 2 Hz).

(e) *With 1-benzoyl-2-(2,2-dimethylpropylidene)hydrazine.* The hydrazine (3.34 g, 16.3 mmol), thionyl chloride (2.92 g, 14.5 mmol), and anhydrous benzene (50 cm^3) heated under reflux for 8 h, gave, on evaporation *in vacuo*, a yellow oil. Distillation of the oil afforded benzoyl chloride (0.1 g) and a red oil (3.1 g) (Found: C, 68.1; H, 7.1; N, 12.5; Cl, 6.9%), b.p. 120 °C at 2 mmHg, shown by ^{1}H n.m.r. (60 MHz) [δ 7—8 (Ar), 1.3 (s, Me_3C × 0.55), and 1.05 (s, Me_3C × 0.45)] to contain two components, one of which was identified (g.l.c.–mass spectroscopy) as 5-phenyl-2-t-butyl-1,3,4-oxadiazole, *m/e* 202 (61%, M^+), 187 (41, M^+ — Me), 145 (3, M^+ — Me_3C), 118 (23), 105 (100), 103 (39), 90 (16), and 77 (70, Ph^+).

Reaction of Thionyl Bromide with Aroylhydrazones.—In a typical reaction, 1-benzoyl-2-(4-chlorobenzylidene)hydrazine (4.0 g, 15 mmol) and redistilled thionyl bromide (3.52 g, 16.9 mmol) were refluxed in dry benzene (150 cm^3) for 8 h. The solution, when cold, deposited crystals of 1,4-bis-(4-chlorophenyl)-2,3-diazabutadiene hydrobromide, which dehydrobrominated when left at 20 °C to give 1,4-bis-(4-chlorophenyl)-2,3-diazabutadiene (1.93 g, 6.9 mmol, 44%) (Found: C, 60.6; H, 3.5; N, 10.4; Cl, 25.6; M^+, 276. Calc. for $C_{14}H_{10}Cl_2N_2$: C, 60.7; H, 3.6; N, 10.1; Cl, 25.6%; *M*, 276), m.p. 211 °C (lit.,[15] m.p. 205—206 °C). The filtrate was concentrated and the deposit which formed was collected and identified as 2,5-diphenyl-1,3,4-oxadiazole (1.5 g, 6.7 mmol, 43%) (Found: C, 75.4; H, 4.6; N, 12.5%; M^+,222. Calc. for $C_{14}H_{10}N_2O$: C, 75.7; H, 4.5; N, 12.6%; *M*, 222), m.p. 137 °C (from aq. EtOH) (lit.,[16] 138 °C). In a similar experiment, 1-benzoyl-2-(4-methylbenzylidene)hydrazine gave the 2,5-diphenyloxadiazole (36%) and 1,4-bis(4-methylphenyl)-2,3-diazabutadiene (40%) (Found: C, 81.1; H, 7.0; N, 11.8%; M^+, 236. Calc. for $C_{16}H_{16}N_2$: C, 81.4; H, 6.8; N, 11.9%; *M*, 236), m.p. 157 °C (lit.,[17] m.p. 157 °C).

Reactions of 1-Chloro-1,4-diaryl-2,3-diazabutadienes.—(a) *With potassium thiocyanate.* In a typical reaction, potassium thiocyanate (3.8 g, 39 mmol) and the appropriate 1-chlorodiazabutadiene (39 mmol) were vigorously stirred in dry ethanol (100 cm^3) at 60 °C (30 min). The solution was filtered hot to remove potassium chloride, concentrated *in vacuo* to *ca.* 25 cm^3, and cooled to −25 °C. The 1-thiocyanato-1,4-diaryl-2,3-diazabutadiene (12) was collected and recrystallized from ethanol. Yields and elemental and ^{1}H n.m.r. data for the thiocyanatodiazabutadienes (12) are listed in SUP 22909.

(b) *With thiosemicarbazide.* In a typical experiment, 1-chloro-1,4-diphenyl-2,3-diazabutadiene (1a) (7.0 g, 29 mmol) and thiosemicarbazide (2.62 g, 29 mmol) were stirred in dry ethanol (100 cm^3) at 55 °C for 1.5 h, and the solution was concentrated *in vacuo* to *ca.* 50 cm^3. The concentrate was kept at −25 °C (12 h), and the resulting precipitate was recrystallized (EtOH) and identified by mixed m.p. with an authentic sample, prepared as described below, as 2-benzylidenehydrazino-5-phenyl-1,3,4-thiadiazole (5.4 g, 66%). Analytical data, yields, m.p.s, and n.m.r. data of new arylidenehydrazino-5-aryl-1,3,4-thiadiazoles (16) obtained in this way are listed in SUP 22909. Authentic 2-benzylidenehydrazino-5-phenyl-1,3,4-thiadiazole was prepared by condensation of benzaldehyde (10 mmol) with 2-hydrazino-5-phenylthiadiazole (17) (10 mmol) in refluxing ethanol, and was isolated (73%), on cooling the solution to −25 °C (Found: C, 64.4; H, 4.6; N, 19.9; S, 11.2%; M^+, 280. Calc. for $C_{15}H_{12}N_4S$: C, 64.3; H, 4.3; N, 20.0; S, 11.4%; *M*, 280), m.p. 248 °C (lit.,[8] 256 °C).

(c) *With thiocarbohydrazide.* A mixture of the 1-chlorodiphenyldiazabutadiene (1.14 g, 4.7 mmol) and thiocarbohydrazide (0.5 g, 4.7 mmol) was stirred in dry ethanol (50 cm^3) for 30 min at 58 °C. Evaporation gave a residue which was recrystallized from ethanol, yielding 2-benzylidenehydrazino-5-phenyl-1,3,4-thiadiazole (1.0 g, 77%), identical with previous samples.

(d) *With potassium ethylxanthate.* A mixture of 1-chlorodiphenyldiazabutadiene (1a) (6.7 g, 28 mmol) and potassium ethylxanthate (4.4 g, 28 mmol) was kept in ethanol at 60 °C (1 h), and then filtered hot to remove potassium chloride. The filtrate was evaporated *in vacuo*, and the residue identified as 1,4-diphenyl-1-ethylxanthyl-2,3-diazabutadiene (19) (7.4 g, 82%) (Found: C, 61.6; H, 4.7; N, 8.5; S, 19.4%; M^+, 328. Calc. for $C_{17}H_{16}N_2OS_2$: C, 62.2; H, 4.9; N, 8.5; S, 19.5%; *M*, 328), m.p. 78—79 °C (lit.,[9] 80—81 °C).

(e) *With 2-aminobenzenethiol.* 1-Chlorodiphenyldiazabutadiene (1a) (5.2 g, 21 mmol) and 2-aminobenzenethiol (5.36 g, 43 mmol) were kept at 60 °C for 30 min in dry ethanol (50 cm^3). The solution was concentrated *in vacuo*, and the white precipitate was recrystallized from aqueous ethanol and identified spectroscopically as 2-phenylbenzothiazole (22) (3.58 g, 81%) (Found: C, 73.7; H, 4.3; N,

6.6; S, 15.4%; M^+, 211. Calc. for $C_{13}H_9NS$: C, 73.9; H, 4.3; N, 6.6; S, 15.2%; *M*, 211), m.p. 115 °C (lit.,[18] 115 °C).

Thermal Isomerization of 1,4-*Diaryl*-1-*thiocyanato*-2,3-*diazabutadienes* (12).—In a typical experiment, the compound (12) (4.5 mmol) was heated in anhydrous xylene (20 cm³) under reflux for 7 h; the solution was then cooled to −25 °C and the resulting precipitate recrystallized from ethanol to give the corresponding 2-arylideneamino-5-aryl-1,3,4-thiadiazole (13) (yields, m.p.s and elemental analytical data, and ^{1}H n.m.r. data are included in SUP 22909). The filtrates, when evaporated, gave unidentified yellow amorphous powders.

Hydrolysis of 2-*Benzylidenehydrazino*-5-*phenyl*-1,3,4-*thiadiazole* (16).—The thiadiazole (16) (0.35 g, 1.25 mmol) and concentrated hydrochloric acid (10 cm³) were refluxed for 16 h (the thiadiazole had been shown to be resistant to hydrolysis in aqueous ethanolic hydrochloric acid). The solution was cooled for 15 h and the white precipitate washed and recrystallized from aqueous ethanol and identified as 5-phenyl-1,3,4-thiadiazol-2(3*H*)-one (0.14 g, 63%) (Found: C, 53.6; H, 2.9; N, 15.9; S, 18.2%; M^+, 178. Calc. for $C_8H_6N_2SO$: C, 53.9; H, 3.4; N, 15.7; S, 18.0%; *M*, 178), m.p. 146—147 °C (lit.,[7] 147—148 °C).

Pyrolysis of 1,4-*Diphenyl*-1-*ethylxanthyl*-2,3-*diazabutadiene* (19).—The diazabutadiene (19) was recovered unchanged after 48 h in refluxing xylene. A sample (0.4 g, 1.2 mmol) kept in a sealed Pyrex tube (100 cm³) at 240 °C for 20 h, gave 2,5-diphenyl-1,3-4-thiadiazole (20) (0.2 g, 69%), m.p. and mixed m.p. with an authentic sample 141—142 °C, and carbon oxygen sulphide which was identified by i.r. analysis of the volatile products.

We are indebted to the S.R.C. for a grant (to J. F. R.)

[0/180 *Received*, 31st *January*, 1980]

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