The Mechanism of Cyclization of 1,4-Diaryl-1-azido-2,3-diazabuta-1,3-dienes to Tetrazoles. Imidoyl Azides stabilized by Slow Nitrogen Inversion [1]

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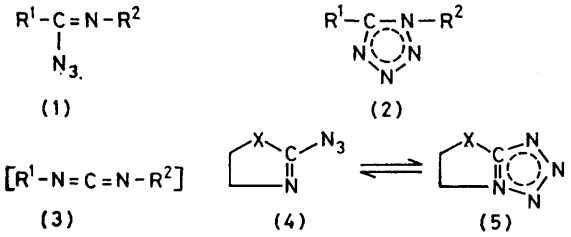
The imidoyl azides (9) are stabilized in the open chain azido form because of their configuration (which is *Z* about the C=N bond) and slow *ZE* isomerisation. The rates of conversion of the azides (9) into the isomeric tetrazoles (12) have been measured and are characterized by a low sensitivity to solvent, a larger substituent effect for the remote substituent Y than for the adjacent X (ρ_Y +1.45, ρ_X −0.28 in toluene at 70°), $\Delta S^{\ddagger}$ −6 cal mol^{-1} K^{-1}, and insensitivity to catalysts. All these data point to nitrogen inversion, rather than the azide cyclization step itself, as rate determining. The *E*-azide was not detected and presumably cyclizes to (12) rapidly. The general applicability of these results to other open-chain azides is discussed.

ONE of the puzzling features of the equilibrium between open chain imidoyl azides (1) and cyclic tetrazoles (2) is that although theoretical calculations [2] predict that the tetrazole form is far more stable, many examples are known in the literature of azides which resist all attempts to induce them to cyclize.[3] Furthermore, in some cases both the azide and tetrazole forms are known (being formed *via* different synthetic routes), but do not interconvert,[4–7] suggesting a high energy barrier between the two forms. No entirely satisfactory explanation of this phenomenon has been offered to date.

We therefore set out to examine the mechanism of cyclization of an azido system, which although isolable, could be converted under mild conditions to the corresponding tetrazole. The range of such substrates available for study is quite limited since the majority of imidoyl azides spontaneously cyclize, even at low temperature.[3,8] On the other hand, other azides are so stable that on heating in an inert or hydroxylic solvent or on treatment with acid, rearrangement to the carbodiimide (3) (which is normally isolated as an adduct with the solvent) occurs rather than cyclization.[4,5]

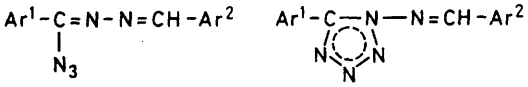
Thus, to date, studies on systems in which both forms



(1) (2) (3) (4) (5)

are detectable have been limited to imidoyl azides in which the C=N function is itself part of a ring (4).[9–15] Ring-strain in the bicyclic tetrazole form (5) can ensure that both forms coexist in solution and a simple correlation, between the size of the ring containing the C=N group (*i.e.* the nature of the linking atom or group X) and the stability of the tetrazole, has been observed.[3] However, ring-strain effects tend to dominate the position of the equilibrium making the separation of electronic effects difficult.[9,10]

Stolle [16] has reported that the 2,3-diazabuta-1,3-diene system can be prepared in both azido (6) and tetrazole (7) forms and that interconversion (6) ⟶ (7) occurs under mild conditions on heating. We have therefore used this system to examine the factors which govern the stability of the azido form and the rate of conversion to



(6) (7)

the tetrazole. Ring-strain effects are absent in this system and systematic variation of substituents attached to carbon (Ar^1) and nitrogen (Ar^2) is possible.

RESULTS AND DISCUSSION

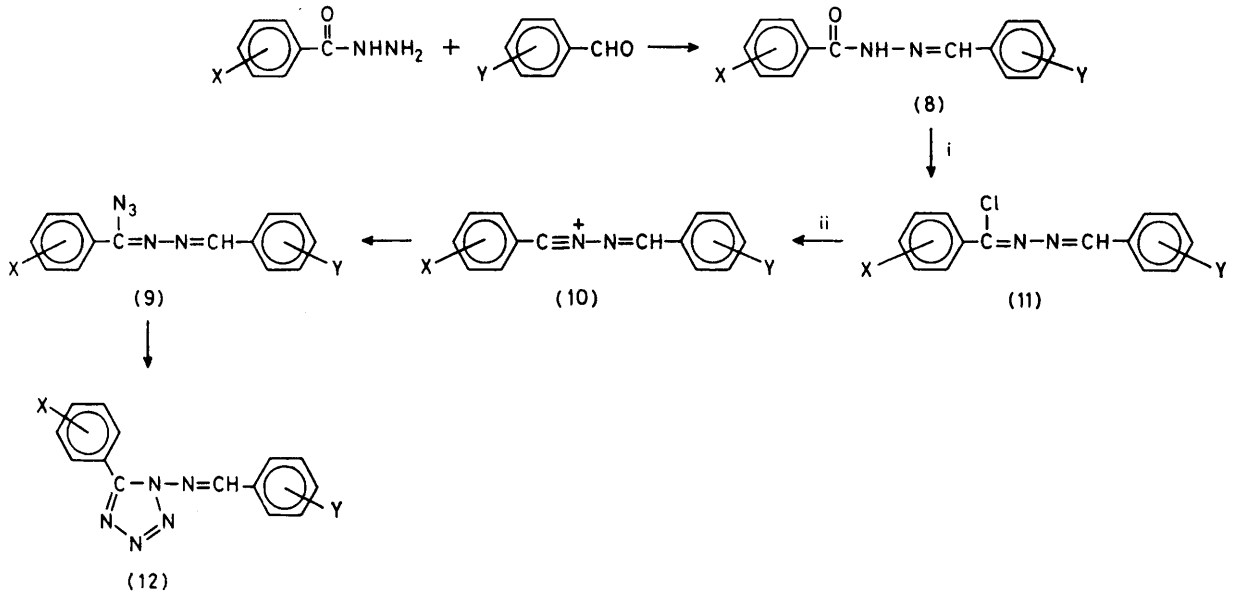
The required azides (9) were prepared by the general route shown in Scheme 1. Chlorination of the hydrazide (8) by thionyl chloride gave the monochlorides (11) in good yield even when the group X was activating (*e.g.* X = *p*-MeO), contrary to earlier reports.[17] Direct solvolysis of the chloride at 50—60° in 1 : 1 acetone–water in the presence of an excess of azide ion gave the imidoyl azides (9) directly. Stolle [16] used an alternative route to the azides, treatment of the chloride with hydrazine, followed by diazotization. We have confirmed that the materials prepared by both routes (9; X = Y = H) are identical.

On heating in inert solvents the azides (9) were smoothly converted to the corresponding tetrazoles. On cyclization the characteristic azide absorption at 2 100 cm^{-1} disappeared and the u.v. absorption at 320 nm was replaced by a tetrazole absorption at 300 nm (12; X = Y = H). The low-melting azides had characteristic m.p.s distinct from those of the tetrazoles; however high-melting azides had apparent m.p.s which were the same as those of the tetrazole. Presumably in the latter case azide–tetrazole interconversion occurred before melting.

Solvent Effects.—The rate of cyclization of (9; X = H, Y = *p*-NO_2) was examined in a variety of solvents by following the decrease in the azide absorption at 380

nm. The results are summarized in Table 1, and show a remarkable insensitivity to solvents as disparate as toluene and DMSO. Because of the small change in reaction rate with any solvent parameter, no further correlation of the results was attempted.

rate of cyclization of the azides (9) was examined in toluene at 70° (see Table 2). Clearly substituents X in the ring adjacent to the azido group have a minor effect on the rate while the effect of remote substituents Y is substantial. This is shown in the Hammett plot



SCHEME 1 Reagents: i, $SOCl_2$; ii, NaN_3 in 1 : 1 Me_2CO–H_2O, 70°

Acid or Base Addition.—The azide ⟶ tetrazole cyclization was also insensitive to the addition of small quantities of acid or base, being pH independent over a wide region. This is an advantage relative to other imidoyl systems which undergo catalysed hydrolysis, isomerization, *etc.* This arises since the azides (9) are relatively non-basic, being unprotonated even in 0.1M-acid.

Addition of acid or base, however, did promote competing hydrolysis of the azide, but this was relatively slow. For example, in 1 : 1 ethanol–water at 60° in the presence of either 0.01M-HCl or -KOH, the rate of cyclization of the azide (in neutral solutions). Thus under the neutral solvent conditions used cyclization to the tetrazole is both uncatalysed and solvent independent.

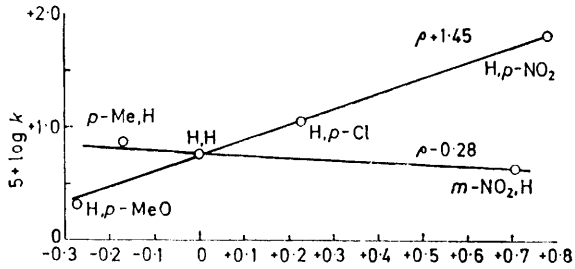
TABLE 1

Rate constants for the cyclization of azides (9) [a] to (12) [a] as a function of solvent

Solvent	ε [b]	$10^4 k_{obs.}$ [c]/s^{-1}
Methylcyclohexane	2.020	1.88
Dioxan	2.209	1.97
Carbon tetrachloride	2.238	2.03
Toluene	2.379	1.93
Chlorobenzene	5.62	3.49 [d]
Ethanol	24.30	2.56
Dimethylformamide	36.7	2.045
Dimethyl sulphoxide	48.9	2.60

[a] X = H, Y = 4-NO_2. [b] 'Advances in Linear Free Energy Relationships,' ed. J. Shorter and N. B. Chapman, Plenum Press, London, 1972, ch. 5. [c] At 60 °C, measured at 380 nm. [d] See text.

Substituent Effects.—The effect of substituents on the rate of cyclization of the azides (9) was examined in toluene at 70° (see Table 2). Clearly substituents X in the ring adjacent to the azido group have a minor effect on the rate while the effect of remote substituents Y is substantial. This is shown in the Hammett plot in the Figure, where ordinary McDaniel–Brown σ values [18] are used to correlate the data giving ρ_X −0.28 and ρ_Y +1.45. The use of other substituent scales (*e.g.* σ^+ or σ^-) significantly increased the scatter of the plot for Y substituents. The effect of temperature on the rate of azide–tetrazole cyclization was also examined using (9; X = H, Y = *p*-NO_2) as substrate; these results give a $\Delta S^‡$ −6 cal mol^{-1} K^{-1} and $\Delta H^‡$ 23.1 kcal mol^{-1}.



Hammett plot for the cyclization of the azides (9) to the tetrazoles (12) as a function of substituents (X,Y); the slopes (or ρ values) are ρ_X −0.28 and ρ_Y +1.45

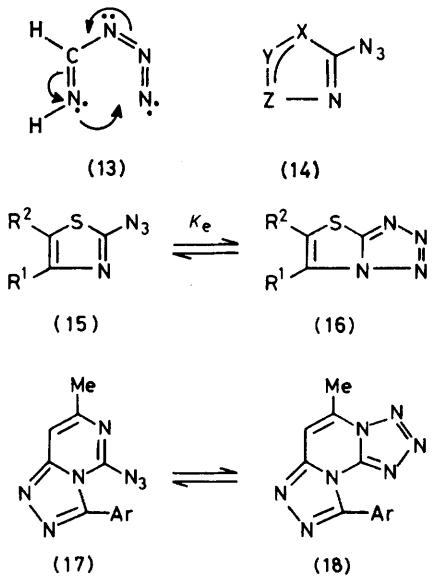
TABLE 2

First-order rate constants for the cyclization of the azides (9) ⟶ (12) at 70 °C

X	Y	$10^5 k_{obs.}$ [a]/s^{-1}
H	*p*-OCH_3	1.88
H	H	5.8
H	*p*-Cl	10.4
H	*p*-NO_2	63.0
m-NO_2	H	4.01
p-CH_3	H	7.43

[a] At 70 °C, in dry toluene.

Mechanism.—The kinetic results are clearly inconsistent with a mechanism involving rate-determining cyclization of the azide to the tetrazole. Theoretical

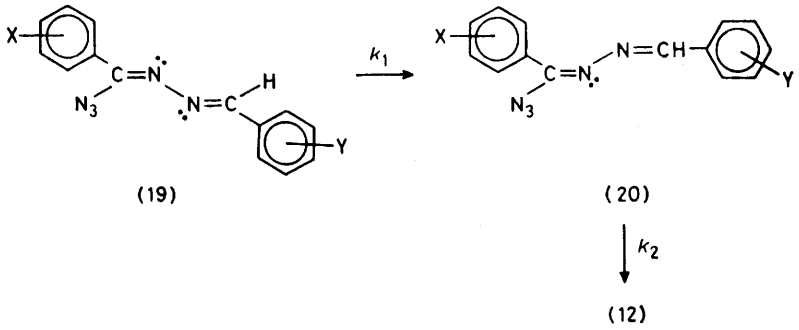


studies have shown [2] that this cyclization step involves the lone pair on the imidoyl nitrogen moving towards the azido group as the latter is bent from its preferred linear structure (13). Since the transition state is more polarized with respect to the starting azide, it is predicted that cyclization will be accelerated in polar solvents [contrary to the effect observed for (9)]. There is some experimental evidence which supports this conclusion *e.g.* for azides of type (14) a large effect of polarity and basicity of the solvent is noted; an increase in either shifts the equilibrium to the tetrazole form.[11]

It is also predicted [2] that electron-donating substituents attached to nitrogen would aid reaction (increasing electron density thus aiding nucleophilic attack). Again evidence comes from cyclic materials (14) to support this, at least as far as equilibrium studies between the azido and tetrazole forms are concerned. Faure and his co-workers [12] report ρ values of +12.6 (for R^1, correlation with σ_m) and 3.75 (for R^2, correlation with σ_p) for the equilibrium constants K_e = [Azide]/[Tetrazole], [(15)]/[(16)], for the thiazoles (15). The same trend is noted [10] in the position of the equilibrium between (17) and (18) in trifluoroacetic acid, but an unusual direct correlation between K_e (rather than log K_e) and σ is noted (with slope +1.16), as the group Ar is varied.

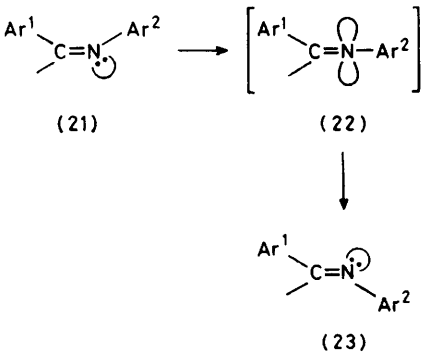
The large rate *enhancement* by electron-withdrawing substituents Y, together with the relative insensitivity to substituents X in the conversion of (9) into (12) are clearly not consistent with rate-determining cyclization of the imidoyl azide. We therefore propose that the slow step of this reaction is a necessary inversion of the imidoyl nitrogen which occurs prior to cyclization (Scheme 2). The correctness of this mechanism implies that (a) the substituent, solvent, and thermodynamic effects observed are for k_1, a nitrogen inversion, rather than for k_2 and (b) that the initial azido substrate has the configuration (19) and that *Z–E* isomerization, (19) ⟶ (20), is conceivably slow enough to permit it to be rate-determining.

The rates of nitrogen inversion in imidoyl systems have been widely studied and for simple imine systems such as (21) it is clear that the major mechanistic pathway is *via* a lateral shift of the *N*-aryl substituent (Ar^2) through a linear transition state (22). This inversion mechanism is characterised by very low substituent effects for aryl groups attached to carbon with ρ values in the region



SCHEME 2

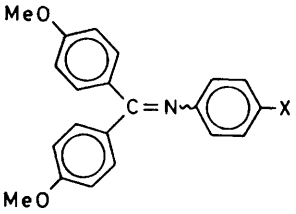
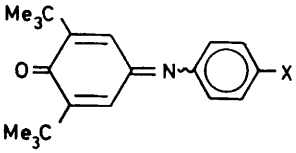
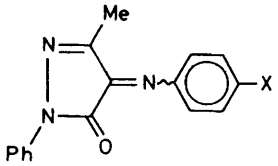
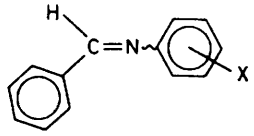
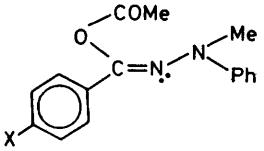
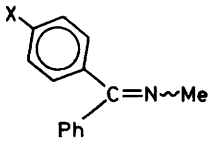
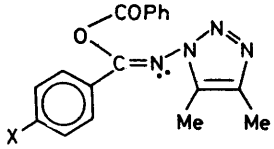
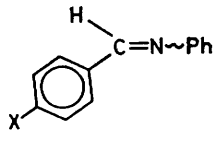
0 ± 0.5 (see Table 3). Substituents in Ar^2 however are reported to have large positive ρ values, inversion



being aided by electron-withdrawing substituents (see Table 3).

TABLE 3

Substituent effects on *C*- and *N*-aryl rings for imine *Z*–*E* isomerization

System	N-Aryl substituents (X)	ρ
	H CH_3 $N(CH_3)_2$ $COOC_2H_5$	+1.5 [a]
	H OCH_3	+1.5 [b]
	Electron withdrawing	+1.88 [c]
	$N(CH_3)_2$ OCH_3 CH_3 Cl Br	+2.0 [d]
	C-Aryl substituents H *p*-NO_2	−0.18 [e]
	Cl NO_2	+0.14 [f]
	H OCH_3 CH_3 Cl NO_2	+0.34 [g]
	$N(CH_3)_2$ OCH_3 CH_3 H Cl Br NO_2	+0.40 [d]

[a] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, 1966, **88**, 2775. [b] A. Reiker and H. Kessler, *Tetrahedron*, 1967, **23**, 3723. [c] W. C. Herkstroeter, *J. Amer. Chem. Soc.*, 1973, **95**, 8686. [d] G. Wettermark, *Arkiv. Kemi*, 1967, **27**, 159; G. Wettermark, *J. Phys. Chem.*, 1965, **69**, 1584. [e] M. K. Brady and A. F. Hegarty, unpublished results. [f] D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, 1961, **83**, 3474. [g] W. Kehrback and N. E. Alexandrou, *J. Heterocyclic Chem.*, 1979, **16**, 571.

Although the rates of nitrogen inversion of diazabutadiene systems have not been investigated directly, it is likely that they show a similar response to substituent variation observed with imines. Clearly therefore the ρ values observed (ρ_X −0.28, ρ_Y +1.45) for the conversion of (9) into (12) are characteristic of those expected for k_1, the nitrogen inversion step. The substituent Y acts on the inverting nitrogen through the intervening −N=CH− group which will attenuate the effect of the substituent. Attenuation factors of 0.47 and 0.53 have previously been reported [19,20] for the −CH=CH− and −N=N− (both *trans*) groups and assuming a similar factor for −N=CH− would give a ρ_Y value for nitrogen inversion of +3.0, comparable to values measured directly for Ar² in simple imines (21).

The low sensitivity to solvent effects (see Table 1) is also characteristic of uncatalysed nitrogen inversions as is the observed entropy of activation. The unusual faster rate in the chlorinated solvent (chlorobenzene, see Table 1) also has a precedent since the same effect has been noted in uncatalysed isomerization of oximes, imines, and hydrazones.[21]

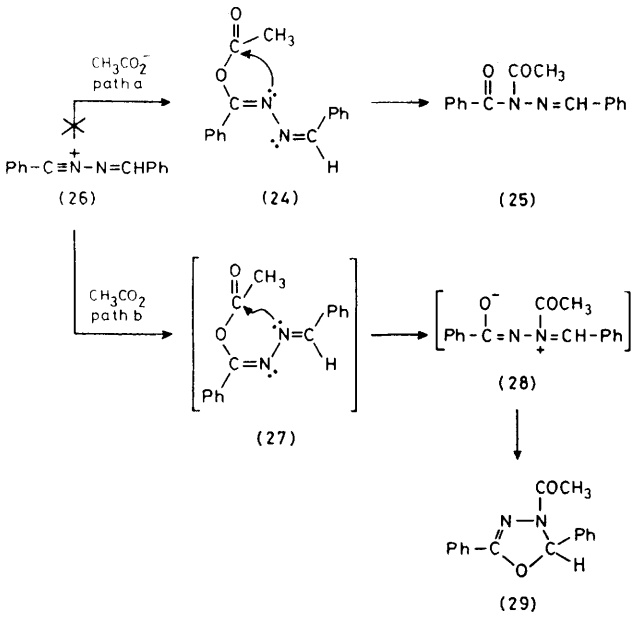
The diazabutadiene (19) has two imino nitrogens capable of undergoing inversion. It is not known whether the aldimine nitrogen or the imidoyl azide nitrogen (as written in Scheme 2) undergoes inversion most readily. Simultaneous inversion of both nitrogens is unlikely, however, since a similar response to substituents X and Y would then be expected. This does not however rule out rapid prior inversion of the aldimine nitrogen since only when the imidoyl azide nitrogen inverts [to (20)] does trapping by the adjacent azido group occur.

The mechanism of Scheme 2 implies that the diazabutadiene has the *Z* configuration about the imidoyl azide C=N bond. This is almost certainly true since it has been shown [22] that nitrilium ions (−C≡$\overset{+}{N}$−) and nitrile oxides (−C≡$\overset{+}{N}$−$\bar{O}$) react with nucleophiles to give stereospecifically the product in which the incoming nucleophile and the forming lone pair on the adjacent nitrogen are mutually *trans*. There are no known exceptions to this and theoretical calculations on the nitrile oxide reaction suggest a large energy difference (*ca.* 60 kcal mol^{-1}) in the transition states for the formation of both isomers.[22] The formation of the azide (9) was carried out under conditions known [23] to involve the nitrilium ion (10); trapping of this by azide ion should give the *Z*-azide (19).

We have confirmed that trapping of the nitrilium on (10) leads to a *Z*-product using acetate as nucleophile. Under conditions similar to those used for the formation of (19) [*viz.* treatment of the chloride (10) in 1 : 1 acetone–water at 70°] but using sodium acetate in place of sodium azide, the *N*-acyldihydro-oxadiazole (29) was the sole product isolated. This is unequivocal evidence that trapping of the nitrilium ion (26) initially gives the *Z*-acetate (27) (path b); acyl group rearrangement to the remote aldimine nitrogen then occurs giving (28), which

then cyclizes to the observed product (29). The alternative (path a) would give an *O*-acylamide (24) which would be either isolable as such or on rearrangement to the adjacent nitrogen [giving the *N*-acylamide (25)].[24]

In conclusion, then, the imidoyl azides (19) have the *Z*-configuration about the C=N bond and initial nitrogen inversion is required prior to cyclization. These azides are therefore stable in the open-chain form, not because of slow cyclization, but because nitrogen inversion is relatively slow in these systems. This is most likely a very general result since those imidoyl azides in which nitrogen inversion should be fast (such as simple *N*-arylimidoyl azides) invariably cyclize spontaneously to the tetrazole form. Since the slow step for the conversion of (9) into (12) is nitrogen inversion (the azido



group merely trapping one isomer) and the overall reaction is accompanied by a large spectral change, the system is particularly useful for investigating the transmission of substituent effects in nitrogen inversions.

EXPERIMENTAL

M.p.s were determined on a Thomas Hoover capillary apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. The solvents used were either spectroscopic grade or purified before use, using standard literature procedures.[25] Solvent mixtures were prepared by mixing appropriate volumes of the components. Sodium azide was laboratory grade (B.D.H.) and thionyl chloride was distilled immediately before use.

Substrates.—The synthesis of the benzohydrazides (8) has been described previously.[23]

1,4-Diaryl-1-chloro-2,3-diazabutadienes (11) were prepared by refluxing the benzohydrazides (8) overnight, in dry benzene, with a slight excess of thionyl chloride. Despite a previous report [17] to the contrary we were also able to synthesise 1-chloro-4-(4-methoxyphenyl)-1-phenyl-2,3-diazabutadiene (11; X = H, Y = 4-OCH_3) by this method. 4-Methoxybenzylidenebenzohydrazide (34.0 g, 0.13 mol) and an excess of thionyl chloride (11 ml, 0.15 mol) were heated under reflux, for 6 h, in dry benzene (300 ml). The solution was then concentrated to *ca.* 100 ml under reduced pressure. On cooling a yellow solid precipitated and this was identified as the starting benzohydrazide. Further cooling of the filtrate yielded an orange precipitate. Some of this material dissolved in light petroleum (b.p. 60—80°) on heating. The insoluble material was filtered off and on cooling of the filtrate, a yellow solid precipitated out of solution. This was found to be the desired *chloride*, m.p. 85—87 °C (Found: C, 65.9; H, 4.9; Cl, 12.1; N, 10.2. $C_{15}H_{13}ClN_2O$ requires C, 66.1; H, 4.8; Cl, 13.0; N, 10.3%).

1,4-*Diaryl*-1-*azido*-2,3-*diazabutadienes*.—The following is typical of the procedure used to synthesise all the azides. 1-Chloro-4-(4-nitrophenyl)-1-phenyl-2,3-diazabutadiene (0.50 g, 0.001 7 mol) was dissolved in acetone (50 ml) and the solution heated to *ca.* 50 °C. To this was added, over 10—20 min, sodium azide (0.81 g, 0.012 mol) in water (50 ml). When all the sodium azide was added, the solution was heated to 60° for 1 h. More acetone was added during this time to prevent precipitation. The solution was then placed in an ice-bath and a light green solid precipitated out of solution, which had m.p. 224—226 °C (Found: C, 56.8; H, 3.4; N, 28.1. $C_{14}H_{10}N_6O_2$ requires C, 57.1; H, 3.4; N, 28.6%), $\nu_{max.}$ 2 140, 2 100 ($-N_3$), and 1 593 cm^{-1} (C=N).

Slightly longer reaction times and higher temperatures were required to synthesise some of the other azides. The analytical data for the azides are summarized in Table 4.

The corresponding tetrazoles (12) were synthesised as follows: 1-azido-4-(4-chlorophenyl)-1-phenyl-2,3-diazabutadiene (0.14 g, 0.000 5 mol) was refluxed in ethanol (25 ml) for 24 h. The ethanol was then removed under reduced pressure and the crude *tetrazole* remaining was recrystallized a number of times from benzene–light petroleum (b.p. 40—60°), m.p. 171—173 °C (Found: C, 58.8; H, 3.7; Cl, 12.5; N, 24.2. $C_{14}H_{10}ClN_5$ requires C, 59.3; H, 3.5; Cl, 12.5; N, 24.7%).

The i.r. spectrum had no absorptions between 2 200—2 050 cm^{-1}, indicating that there was no azide present.

TABLE 4

Physical data for the azides (9)

Substituent		Empirical formula	M.p. (°C)	Found (%)			Required (%)		
X	Y			C	H	N	C	H	N
H	H	$C_{14}H_{11}N_5$	57—61	67.3	4.4	28.0	67.5	4.4	28.1
H	4-NO_2	$C_{14}H_{10}N_6O_2$	224—226	56.8	3.4	28.1	57.1	3.4	28.6
H	4-OCH_3	$C_{15}H_{13}N_5O$	88—92	64.4	4.6	24.9	64.5	4.7	25.1
4-Me	H	$C_{15}H_{13}N_5$	99—102	67.7	5.0	26.0	68.4	4.9	26.6
3-NO_2	H	$C_{14}H_{10}N_6O_2$	111—113	57.4	3.6	28.2	57.1	3.4	28.6

3-*Acetyl*-2,3-*dihydro*-2,5-*diphenyl*-1,3,4-*oxadiazole* (29).—Benzylidenebenzohydrazide (4.78 g, 0.02 mol) and acetic anhydride (50 ml, 0.53 mol) were refluxed for 3 h. The excess of acetic anhydride was removed by vacuum distil-

lation, leaving a light brown oil. The oil was slurried with light petroleum (b.p. 40—60) and the insoluble solid obtained was recrystallized from 95% ethanol, m.p. 84—86° (lit.,[26] 98—99°), δ 2.27 (s, $COCH_3$), 7.07 (1 H, s), and 7.4 (m, $-C_6H_5$) (Found: C, 72.1; H, 5.4; N, 10.6. Calc. for $C_{16}H_{14}N_2O_2$: C, 72.2; H, 5.3; N, 10.5%).

Kinetic Method.—(a) *The azide–tetrazole cyclization.* The course of the reaction was followed on a Unicam SP 800, a Perkin-Elmer 124, or a Beckman model 25 u.v. spectrophotometer. Repetitive scans of the u.v. region established suitable wavelengths at which an appreciable optical density change occurred during the course of the reaction. Reactions were initiated by injecting 10—15 μl of the substrate (1×10^{-2}M), in sodium-dried toluene, into a cell containing dry toluene. This cell was equilibrated for 15 min before each kinetic run, at the reaction temperature. Good pseudo-first-order rate constants were obtained using experimental infinity values.

(b) *Stereospecific trapping of the nitrilium ion* (26). The hydrolysis of the chloride (11; X = Y = H) was followed at a suitable wavelength in the u.v. region [23] on a Beckman model 25 u.v. spectrophotometer using 1 : 1 dioxan–water as solvent at 55°. The rate of hydrolysis of the chloride was noted both in the absence of added salt [where the product was the hydrazide (8; X = Y = H)] and in the presence of 0.1M-sodium acetate where the product was shown to be the oxadiazole (29). Reactions were initiated by injecting 5 μl of the chloride substrate (11; X = Y = H) (5×10^{-2}M) in purified dioxan, into this cell.

Product Analysis.—The products obtained from the azide isomerisation and the nitrilium ion trapping were confirmed to be the tetrazole and the oxadiazole, respectively, by independent synthesis and comparison. U.v., i.r., and n.m.r. spectra of authentic samples of the tetrazole and oxadiazole were identical with the products obtained on completion of the kinetic experiments.

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