Chemistry of Polyhalogenodiazabutadienes. Part IV.[1] The Synthesis of Dihalogeno- and Trihalogeno-diazabutadienes

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Reaction of arylmethylene(tetrazol-5-yl)hydrazines (VI) with bromine in aqueous acetic acid leads to tetrazolyl ring cleavage with formation of the 1,1-dibromo-2,3-diazabutadienes ($ArCH{:}N{\cdot}N{:}CBr_2$) (II). This reaction involves initial *N*-bromination, loss of HBr to give a tetrazol-5-ylidenehydrazine (XII), followed by production of an arylmethyleneamino-isocyanide ($ArCH{:}N{\cdot}NC$), which adds bromine to yield the 4-aryl-1,1-dibromo-2,3-diazabutadienes (II). Chlorination of the hydrazines (VI) in aqueous acetic acid yields the 1,1,4-trichloro-2,3-diazabutadienes ($ArCCl{:}N{\cdot}N{:}CCl_2$) (IV), *via* the intermediate hydrazonyl chlorides (VII). The corresponding tribromo-compounds (V) are prepared similarly, through the intermediacy of the hydrazonyl bromides (VIII). The tribromides cannot be prepared from the dibromodiazabutadienes (II).

SYNTHETIC products from polyhalogenodiazabutadienes depend upon the location, number, and kind of halogen atoms concerned. For example, reaction of 1,4-dichloro-2,3-diazabutadienes (I) (products of the chlorination of symmetrical aldehyde azines [2]) with nucleophiles (such as hydroxide ion or primary amines) leads to oxadiazoles [2a,3] or 1,2,4-triazoles.[4] We now describe the synthesis of two new series of halogenodiazabutadienes, which enhance the flexibility of heterocyclic syntheses.

$ArCX{:}N{\cdot}N{:}CXY$ $ArCH{:}N{\cdot}N{:}CBr_2$ $ArCH{:}N{\cdot}N{=}$ (X, Y)

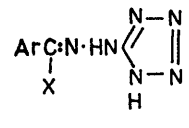
(I) Ar = Y, X = Cl (II) (III)
(IV) X = Y = Cl
(V) X = Y = Br

The first of these are the 4-aryl-1,1-dibromo-2,3-diazabutadienes (II). Their utility lies in the reactivity of the *gem*-dibromo-site towards bifunctional ligands (such as ethylenediamines) to form the heterocyclic hydrazones (III), in an analogous manner to that developed by Kuehle with isocyanide dichlorides ($RN{:}CX_2$).[5]

Much more significant for synthetic purposes are the second group, the 4-aryl-1,1,4-trihalogeno-2,3-diazabutadienes (IV) and (V). Displacement of one halogen atom of the geminate pair with one nucleophile, subsequent replacement of the other by a different nucleophile, followed by ring-closure allows considerable flexibility in the building of polyaza-ring systems, which we shall exemplify in subsequent papers. Herein we confine ourselves to the syntheses of the key intermediates (II), (IV), and (V).

RESULTS AND DISCUSSION

Halogenation of arylmethylenehydrazines (VI) leads mainly to the corresponding hydrazonyl halides ‡ (VII) and (VIII).[6] Thus treatment of compounds (VI) with one equiv. of bromine in glacial acetic acid gives the hydrazonyl bromides (VIII). Addition of water (as an aid to work-up) precipitated the hydrazonyl bromides but also resulted in the formation of quantities of the dibromides (II). The yields of dibromides (II) were optimised by the slow addition of bromine (2·5 equiv.) to



(VI) X = H
(VII) X = Cl
(VIII) X = Br

$ArCH{:}N{\cdot}NH{\cdot}C(NHPh){:}NPh$ (IX)

$Ph_2C{:}N{\cdot}N{:}CBr_2$ (X)

a suspension of the tetrazol-5-ylhydrazine (VI) in acetic acid–water (1 : 2) (addition of the halogen at a rate faster than 1 drop s^{-1} caused extensive hydrolysis of the starting hydrazine), which caused brisk effervescence of nitrogen and the discharging of the bromine colour. During the reaction, the original suspension of hydrazone was replaced by a thick, flocculent precipitate of the dibromide (II) (for physical data see Table 1).

This reaction was not confined to aldehydic hydrazones (VI); benzophenone tetrazol-5-ylhydrazone yielded the corresponding dibromide (X). Other ketonic tetrazol-5-ylhydrazones (such as that of acetophenone) did not yield the desired dibromides under these conditions: hydrolysis occurred instead.

The location of both bromine atoms on the terminal carbon atom in the diazabutadienes (II) was established unequivocally by their reaction in aniline to give the corresponding *N*-(arylmethylene)carbanilohydrazide *N*-phenylimides (IX), identified by unambiguous synthesis. The n.m.r. spectra for two typical dibromides (II; Ar = *p*-ClC_6H_4 and *p*-BrC_6H_4) showed an A_2B_2 pattern for the aromatic protons. Both compounds also gave a single peak for the methine proton at τ 1·72. The chemical shifts of such methine protons are sensitive to structure; signals were observed at τ 1·86 for the hydrazones $ArCH{:}N{\cdot}NHAr$ [7a] and at 1·45 for the azines

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‡ This is the systematic term for compounds to which we have previously referred as hydrazidic halides.

[1] Part III, F. L. Scott and J. K. O'Halloran, *Tetrahedron Letters*, 1970, 4083.

[2] R. Stolle, *J. prakt. Chem.*, (*a*) 1906, **73**, 277; (*b*) 1912, **85**, 386; (*c*) R. Stolle and Fr. Helwerth, *Ber.*, 1914, **47**, 1132.

[3] R. Stolle and A. Bambach, *J. prakt. Chem.*, 1906, **74**, 13.

[4] R. Stolle, *J. prakt. Chem.*, 1906, **73**, 288.

[5] E. Kuehle, *Angew. Chem. Internat. Edn.*, 1969, **8**, 20.

[6] F. L. Scott, D. A. Cronin, and J. K. O'Halloran, *J. Chem. Soc.* (*C*), 1971, 2769.

[7] (*a*) R. N. Butler and F. L. Scott, *J. Org. Chem.* 1966, **31**, 3128; (*b*) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1966, vol. 2, p. 1115.

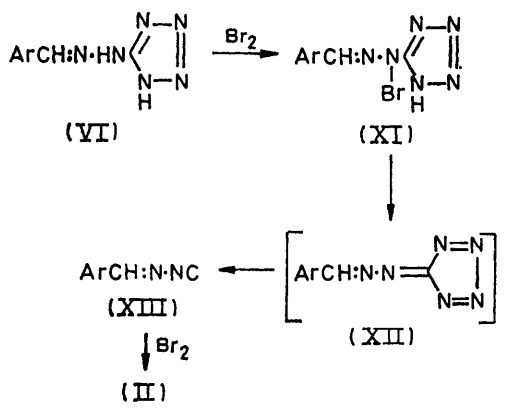
$(ArCH{:}N\cdot)_2$.[7b] It is clear that halogenation of the aromatic ring did not take place.

A preliminary investigation of the kinetics of the bromination was carried out using the electrometric technique we have described previously.[8] The reactions were extremely rapid, in contrast to those carried out with suspensions of the hydrazones. The bromination of benzophenone tetrazol-5-ylhydrazone is first order both in bromine and in hydrazone, $k = 0{\cdot}86$ l mol^{-1} s^{-1} (for methine brominations the rate constants, k, are *ca.* 150 l mol^{-1} s^{-1}). No stepwise disappearance of bromine was evident. Thus it would appear that the rate-determining step involves one molecule of bromine. The bromination of *p*-nitrobenzaldehyde tetrazol-5-ylhydrazone was much faster, with an initial rate constant of 28 l mol^{-1} s^{-1}.

The mechanism of the reaction [equation (1); Tet = tetrazol-5-yl] is of considerable interest. Originally we proposed that the tetrazolyl ring opens to its valence tautomer [$\cdot C(:NH)\cdot N_3$], which then may be reduced to an amidine [$\cdot C(:NH)\cdot NH_2$], which in turn might be converted into the dibromomethylene group. Our studies[9] on the brominations of amidinohydrazones, $ArCH{:}N\cdot NH\cdot C(:NH)\cdot NH_2$, showed that conversions of an amino-amidine into a dibromomethylene group do not occur. Moreover, the availability of a hydrogen atom in the 1-position of the tetrazole ring is vital to the cleavage of the tetrazole ring, since bromination of arylmethylene(1-alkyltetrazol-5-yl)hydrazines does not result in ring cleavage.[10] Based on this evidence we propose the mechanism in Scheme 1.

$$ArCH{:}N\cdot NHTet \longrightarrow ArCH{:}N\cdot N{:}CBr_2 \qquad (1)$$

The first step is *N*-bromination, which is likely to occur at the more basic hydrazine nitrogen atom to give the *N*-bromo-hydrazone (XI). In glacial acetic acid this *N*-bromo-hydrazone can revert back to the parent hydrazone in the presence of bromide ion, whereas the slower methine bromination to form the hydrazonyl bromide (VIII) is irreversible under these conditions. The *N*-bromo-hydrazone loses hydrobromic acid irreversibly to give the unstable tetrazolylidenehydrazone (XII). This step can be blocked by replacement of the 1-hydrogen atom by a methyl group. The hydrazone (XII) loses nitrogen to give an isocyanide (XIII), which then reacts with a second molecule of bromine to give the dibromodiazabutadiene (II).



SCHEME 1

A tetrazole ring cleavage analogous to the conversion described herein has recently been reported by Behringer and Matner,[11] who found that some 5-(halogenodiphenylmethyl)tetrazoles on heating in solution to 150—200 °C underwent ring fission with complete loss of nitrogen to give substituted acetylenes and proposed a mechanism similar to that which we have suggested in Scheme 1.

TABLE 1

Physical data for some 1,1-dibromo-4-phenyl-2,3-diazabuta-1,3-dienes (II)

Substrate Y in Ar = *p*-YC_6H_4	M.p. (°C)	Yield (%)	Formula	Found (%) C	H	N	Br	Required (%) C	H	N	Br
MeO	60—61	85	$C_9H_8Br_2N_2O$	34·0	2·45	8·55	50·3	33·75	2·5	8·75	50·0
H	15—17	19	$C_8H_6Br_2N_2$	33·6	2·2	9·5	54·65	33·1	2·05	9·65	55·15
Cl	92—93	80	$C_8H_5Br_2ClN_2$	30·0	1·65	8·8	48·35	29·6	1·55	8·6	49·3
Br	98—99	75	$C_8H_5Br_3N_2$	25·95	1·55	7·65	64·85	26·0	1·35	7·6	65·05
NO_2	145—147	78	$C_8H_5Br_2N_3O_2$	29·0	1·6	12·7	47·05	28·65	1·5	12·55	47·75

TABLE 2

Physical data for some *N*-(arylmethylene)carbanilohydrazide *N*-phenylimides (IX)

Substrate Y in Ar = *p*-YC_6H_4	M.p. (°C)	Yield (%) from (II)	Yield (%) from unambiguous synthesis	Formula	Found (%) C	H	N	Required (%) C	H	N
MeO	125—126	71	82	$C_{21}H_{20}N_4O$	73·2	6·0	16·5	73·25	5·8	16·3
H	118—119 [a]	47	65	$C_{20}H_{18}N_4$	76·6	5·75	17·6	76·45	5·7	17·8
Cl	151—153	75	85	$C_{20}H_{17}ClN_4$	68·45	5·0	16·0	68·85	4·85	16·05
Br	153—154	68	86	$C_{20}H_{17}BrN_4$	60·65	4·3	14·35	61·0	4·3	14·25
NO_2	155—156	66	90	$C_{20}H_{17}N_5O_2$	66·4	4·75	19·4	66·75	4·75	19·5

[a] Lit.,[19] 120°.

[8] A. F. Hegarty and F. L. Scott, *J. Chem. Soc.* (*B*), 1966, 672.
[9] T. A. F. O'Mahony, unpublished work, this department.
[10] R. N. Butler, F. L. Scott, and D. A. Cronin, *Angew. Chem. Internat. Edn.*, 1965, **4**, 950.
[11] H. Behringer and M. Matner, *Tetrahedron Letters*, 1966, 1663.

An attempt was made to demonstrate the conversion of the isocyanide (XIII) into the dibromide (II) under our conditions by the synthesis and bromination of such an isocyanide. Thus, when potassium hydroxide was added to a solution of benzophenone hydrazone in chloroform, followed by addition of bromine in aqueous acetic acid, reaction occurred to yield the dibromide (X) in 9% overall yield. This material was probably formed by the pathway given in Scheme 2.

$$\underset{\text{(XIV)}}{PhC{:}N{\cdot}NH_2} + {:}CCl_2 \longrightarrow \underset{\text{(XV)}}{Ph_2C{:}N{\cdot}N{:}C{:}} \longrightarrow \text{(X)}$$

SCHEME 2

In an effort to synthesise the analogous dichlorodiazabutadienes (XVI), the tetrazol-5-ylhydrazones (VI) were treated with chlorine in aqueous acetic acid. The only products were the corresponding benzoic acids (30—40%). When Ar was p-MeO·C_6H_4 or p-Pr^iC_6H_4, the by-products were the corresponding p-substituted m-chlorobenzoic acids (20—30%). In the case of the p-methoxy-compound, chlorination of the ring occurred even at the hydrazonyl substitution stage, the tetrachloro-compounds (XVII) being isolated.

A very strong band at 1600 (±5) cm^{-1} in the i.r. spectra of all the trichlorodiazabutadienes (IV) was assigned to C=N stretching vibrations.[12,13] The ^{1}H n.m.r. spectra of these compounds also confirmed their structures: symmetrical A_2B_2 patterns were found for all the compounds (IV) except the p-nitro-substituted compound, indicating that the four protons present were in the aromatic ring. In the case of the p-nitro-compound only one peak (τ 1·78) is observed. One would expect that the p-nitro- and p-CCl:N· substituents would shield their *ortho*-protons equally ('*ortho* effect' for p-NO_2, −0·97 and for p-CCl:O, −0·95 p.p.m.)[14] and it is significant that this signal is 0·95 p.p.m. downfield from that for pure benzene (τ 2·73), indicating that all four protons have been effected. The complicated n.m.r. spectrum of the 1,1,4-trichloro-4-(*m*-chloro-*p*-methoxyphenyl)diazabutadiene (XVII) is what would be expected from trisubstituted benzene derivatives;[15] integration indicates the presence of three protons on the aromatic ring.

TABLE 3

Physical data for the 4-aryl-1,1,4-trichloro-2,3-diazabutadienes (IV)

Substrate Y in Ar = p-YC_6H_4	M.p. (°C)	Yield (%)	B.p. (°C) at 1 mmHg	Formula	Found (%) C	H	N	Cl	Required (%) C	H	N	Cl
Pr^i		58	192—194	$C_{11}H_{11}Cl_3N_2$	47·6	4·2	9·8	38·1	47·5	4·0	9·9	38·7
Me		60	173—174	$C_9H_7Cl_3N_2$	43·6	3·0	10·1	42·4	43·3	2·8	10·1	42·7
H		62	162—164	$C_8H_5Cl_3N_2$	41·2	2·2	11·95	44·6	40·7	2·1	12·0	45·2
Cl	52—54	53		$C_8H_4Cl_4N_2$	35·8	1·6	10·35	52·1	35·55	1·5	10·4	52·5
Br	54—56	55		$C_8H_4BrCl_3N_2$	30·0	1·4	9·2	33·8	30·5	1·2	8·9	33·5
NO_2	79—80	50		$C_8H_4Cl_3N_3O_2$	34·3	1·5	14·6	37·8	34·2	1·4	15·0	37·95

TABLE 4

Physical data for the trimorpholino-2,3-diazabutadienes (XVIII)

Substrate Y in Ar = p-YC_6H_4	M.p. (°C)	Yield (%)	Formula	Found (%) C	H	N	O	Required (%) C	H	N	O
H	127—128	90	$C_{20}H_{29}N_5O_3$	61·8	7·5	18·3	12·35	62·0	7·5	18·1	12·4
Cl	130—131	90	$C_{20}H_{28}ClN_5O_3$	57·2	6·6	16·4	11·1	56·9	6·6	16·6	11·4
Br	129—130	94	$C_{20}H_{28}BrN_5O_3$	51·0	6·3	15·1	10·0	51·5	6·0	15·0	10·3
NO_2	154—155	92	$C_{20}H_{28}N_6O_5$	55·55	6·5	19·6	18·3	55·55	6·5	19·4	18·5

products isolated from reaction in 50—60% acetic acid were the corresponding benzoic acids in 60—70% yields, while the corresponding benzaldehydes were isolated in similar yields from reaction in the less aqueous (70—80%) acetic acid.

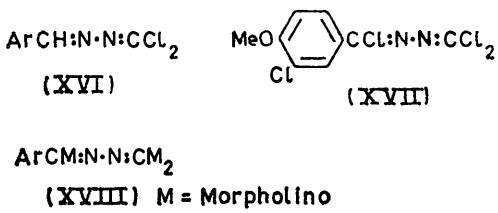
However, when a suspension of p-nitrobenzylidene-(tetrazol-5-yl)hydrazine (VI; Ar = p-NO_2·C_6H_4) in 90% acetic acid was treated with an excess of chlorine gas, the suspension went into solution, and precipitation of the hydrazonyl chloride[6] (VII; Ar = p-NO_2·C_6H_4) occurred. However, if even more gaseous chlorine is added, the suspension again goes into solution. When this solution was added to a large excess of ice-cold water, immediate vigorous effervescence of nitrogen occurred to give the new 1,1,4-trichloro-4-p-nitrophenyldiazabutadiene (IV; Ar = p-NO_2·C_6H_4). Other trichlorodiazabutadienes (see Table 3) were prepared similarly.

These trichloro-compounds were invariably accompanied by products of hydrolysis and oxidation. When Ar was p-NO_2·C_6H_4, p-BrC_6H_4, or Ph, the accompanying

Further evidence for the structures of these trichlorodiazabutadienes (IV) has been obtained from their reaction with morpholine. The fact that the three chlorine atoms are not attached to the ring has been proved conclusively by the formation of the trimorpholino-compounds (XVIII). These were formed, typically, by heating a solution of 1,1,4-trichloro-4-phenyldiazabutadiene (IV; Ar = Ph) in benzene under reflux with

[12] L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' 2nd edn., Methuen, London, 1958, p. 270.
[13] L. D. Frederickson, *Analyt. Chem.*, 1964, **36**, 1349.
[14] L. M. Jackman, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', 1st edn., Pergamon Press, 1959, p. 63.
[15] J. R. Dyer, 'Applications of Absorption Spectroscopy of Organic Compounds,' Prentice-Hall, New Jersey, 1965, p. 107.

6 equiv. of morpholine. Work-up yielded 1,1,4-trimorpholino-4-phenyldiazabutadiene (XVIII; Ar = Ph) (90%).



The tribromodiazabutadienes (V) were prepared in a similar manner to their trichloro-analogues, *i.e.*, by first forming the hydrazonyl bromides (VIII) and by treating these with more bromine in aqueous acetic acid. An attempt to prepare the tribromo-diazabutadienes from the dibromodiazabutadienes (II) by the addition of more bromine failed. Apparently, halogenation at the methine position prior to tetrazolyl ring cleavage is necessary for the formation of the trihalogeno-diazabutadienes (IV) and (V).

EXPERIMENTAL

M.p.s were determined with an Electrothermal apparatus. I.r. spectra were recorded with a Perkin-Elmer Infracord model 137 spectrophotometer with NaCl optics. Solids were examined as KBr discs. ^{1}H N.m.r. spectra were recorded with a Varian HA-100 100 MHz instrument for $CDCl_3$ solutions. Glacial acetic acid, morpholine, and aniline (all B.D.H., AnalaR) were used without further purification. Microanalyses were carried out by Dr. Strauss, Microanalytical Labs., Oxford, and Mrs. K. M. Duggan, Analytical Section, Chemistry Department, University College, Cork.

Benzylidene(tetrazol-5-yl)hydrazines.—The *p*-substituted benzylidene-hydrazines (VI; Ar = *p*-MeO·C_6H_4, *p*-MeC_6H_4, *p*-$Pr^iC_6H_4$, *p*-ClC_6H_4, *p*-BrC_6H_4, and *p*-NO_2·C_6H_4) and (VI; Ar = Ph) were prepared by the previously reported method,[16] except that the tetrazol-5-ylhydrazine was not isolated but treated *in situ* with the appropriate aldehyde in ethanol. The compounds were identical (m.p. and analyses) with those reported previously.

Benzophenone, acetophenone, and *p*-nitroacetophenone tetrazol-5-ylhydrazones were prepared similarly (except that the solution of benzophenone and tetrazol-5-ylhydrazine was heated at 60—70° for 2 h): *benzophenone tetrazol-5-ylhydrazone* (84%), m.p. 217—219° (Found: C, 63·1; H, 4·5; N, 32·4. $C_{14}H_{12}N_6$ requires C, 63·6; H, 4·55; N, 31·85%); acetophenone tetrazol-5-ylhydrazone (87%), m.p. 239—240° (lit.,[17] m.p. 235°) (Found: C, 53·9; H, 4·9; N, 41·2. Calc. for $C_9H_{16}N_6$: C, 53·45; H, 4·95; N, 41·6%); and p-*nitroacetophenone tetrazol-5-ylhydrazone* (65%), m.p. 263—264° (Found: C, 43·7; H, 3·65; N, 39·6; O, 13·25. $C_9H_9N_7O_2$ requires C, 43·7; H, 3·65; N, 39·7; O, 12·95%).

1,1-*Dibromo*-4-*phenyl*-2,3-*diazabuta*-1,3-*dienes* (II).—Typically, to a suspension of *p*-bromobenzylidene(tetrazol-5-yl)hydrazine (VI; Ar = *p*-BrC_6H_4) (5·0 g, 18·7 mmol) in aqueous acetic acid (2 : 1; 150 ml) was added dropwise a solution of bromine (2·5 ml, 48·1 mmol) in glacial acetic acid (15 ml) with vigorous stirring during 1 h. Addition of the bromine was accompanied by a brisk effervescence of nitrogen. The reaction was essentially complete when the colour of the added bromine was no longer discharged, and evolution of gas had ceased. 1,1-*Dibromo*-4-p-*bromophenyl*-2,3-*diazabuta*-1,3-*diene* (II; Ar = *p*-BrC_6H_4), a fluffy white precipitate, was filtered off, washed thoroughly with distilled water, and dried (75%), m.p. 90—93° (from benzene) (Found: C, 26·0; H, 1·55; Br, 64·05; N, 7·65. $C_8H_5Br_3N_2$ requires C, 25·9; H, 1·6; Br, 64·9; N, 7·55%). The other 4-(*p*-substituted phenyl) compounds (II) (see Table 1) were prepared similarly.

The phenyl compound (II; Ar = Ph) was best prepared by isolating it as a by-product in the synthesis of *N*-(tetrazol-5-yl)benzohydrazonyl bromide (VIII; Ar = Ph). Bromination of benzylidene(tetrazol-5-yl)hydrazine (VI; Ar = Ph) (5 g) gave the crude product, which was extracted three times with boiling carbon tetrachloride to yield the pure hydrazonyl bromide (VIII; Ar = Ph) (3·8 g, 53·5%), m.p. 172—174°. The carbon tetrachloride extracts were combined and evaporated. When the residue, a dirty-brown oily material, was extracted several times with small portions (10 ml) of boiling pentane and the pentane extracts were evaporated, a pale green sweet-smelling oil (1·5 g) was obtained. Chromatography [thrice; Woelm (grade 1) alumina; pentane] gave an oil, which, on being cooled with ice–salt and agitated with a glass rod, deposited 1,1-*dibromo*-4-*phenyl*-2,3-*diazabuta*-1,3-*diene* (II; Ar = Ph) (19%), m.p. 15—17° (Found: C, 33·6; H, 2·2; Br, 54·65; N, 9·5. $C_8H_6N_2Br_2$ requires C, 33·1; H, 2·05; Br, 55·15; N, 9·65%).

1,1-*Dibromo*-4,4-*diphenyl*-2,3-*diazabutadiene* (X).—This was prepared as described for the bromination of arylmethylene(tetrazol-5-yl)hydrazines. Filtration gave the diazabutadiene (X) (65%), m.p. 60—62° (Found: C, 46·1; H, 2·75; Br, 43·55; N, 7·7. $C_{14}H_{10}Br_2N_2$ requires C, 45·9; H, 2·75; Br, 43·7; N, 7·65%).

Synthesis of 1,1-*Dibromo*-4,4-*diphenyl*-2,3-*diazabutadiene* (X) *from Benzophenone Hydrazone.*—To a solution of benzophenone hydrazone [18] (2 g, 10 mmol) in chloroform (20 ml) was added potassium hydroxide (1·7 g, 30 mmol) in ethanol (15 ml) and the solution was stirred for 10 min at room temperature. A solution of bromine (1 ml, 20 mmol) in 50% aqueous acetic acid (50 ml) was added and the solution stirred for 1 h at room temperature. The resulting organic layer was separated, diluted with ether, washed with water, dilute sodium carbonate solution, and then with water again until the washings were neutral, and then dried (Na_2SO_4). After evaporation at *ca.* 25° *in vacuo*, the oily residue was extracted with pentane. Evaporation gave the diazabutadiene (X) (9%), m.p. 60—62°, identical (analysis and i.r.) with that prepared above.

Bromination of Acetophenone and p-*Nitroacetophenone Tetrazolylhydrazones.*—Bromination of these hydrazones as described for the arylmethylenehydrazines (VI) followed by filtration gave the starting hydrazine in each case. The filtrates were then neutralised with dilute sodium carbonate solution, extracted with ether, and dried. Evaporation gave the parent ketones, acetophenone and *p*-nitroacetophenone.

[16] F. L. Scott, W. N. Moorish, and J. Reilly, *J. Org. Chem.*, 1957, **22**, 692.

[17] J. Thiele and H. Ingle, *Annalen*, 1895, **287**, 233.

[18] T. Curtius and F. Rauterberg, *J. prakt. Chem.*, 1891, **44**, 192.

N-(*Arylmethylene*)*carbanilohydrazide* N-*Phenylimides* (IX).—Typically, a solution of 1,1-dibromo-4-(*p*-methoxyphenyl)-2,3-diazabutadiene (II; Ar = *p*-MeO·C_6H_4) (700 mg, 2·17 mmol) in ether (30 ml) was heated under reflux with aniline (1·02 ml, 10·85 mmol) for 4 h and the insoluble material was filtered off. The ethereal filtrate was then shaken in a separatory funnel with 10% aqueous ethanol (*ca.* 40 ml), acidified with concentrated HBr (2 ml) to obtain the hydrobromide. The aqueous portion was separated, and made basic with 10% sodium hydroxide solution. On cooling the solution in ice and agitating vigorously, a white precipitate separated. This was filtered off, washed with water, and dried to give N-(p-*methoxybenzylidene*)*carbanilohydrazide* N-*phenylimide* (IX; Ar = *p*-MeO·C_6H_4) (71%), m.p. 126° (from ether–pentane and 95% ethanol) (Found: C, 73·2; H, 6·0; O, 4·3; N, 16·5. $C_{21}H_{20}N_4O$ requires C, 73·25; H, 5·8; O, 4·65; N, 16·3%). Other carbanilohydrazide *N*-phenylimides (IX) were prepared similarly (see Table 2).

Unambiguous Syntheses of N-(p-*Substituted Benzylidene*)-*carbanilohydrazide* N-*Phenylimides* (IX).—These were all prepared by condensing equimolar quantities of the aldehyde and carbanilohydrazide *N*-phenylimide [19] in absolute ethanol. Typically, to a solution of carbanilohydrazide *N*-phenylimide (1 g, 4·4 mmol) in absolute ethanol (8 ml) was added a solution of *p*-bromobenzaldehyde (800 mg, 4·4 mmol) in the same solvent (5 ml). One drop of dilute nitric acid was then added and the solution was warmed gently for a few min. On cooling in ice and scratching, a white precipitate separated. This material was filtered off, washed with 50% ethanol, and dried to give N-(p-*bromobenzylidene*)*carbanilohydrazide* N-*phenylimide* (IX; Ar = *p*BrC_6H_4) (86%), m.p. 155° (from 95% ethanol), identical with the material obtained from the reaction between aniline and the corresponding dibromodiazabutadiene (II; Ar = *p*-BrC_6H_4). The yields of the carbanilohydrazide imides (IX) obtained by this method are also contained in Table 2.

4-*Aryl*-1,1,4-*trichloro*-2,3-*diazabutadienes* (IV).—Typically, to a well-stirred, ice-cooled suspension of benzylidene-(tetrazol-5-yl)hydrazine (VI; Ar = Ph) (10 g, 53 mmol) in 90% aqueous acetic acid (500 ml) was added an excess (*ca.* 1 : 5 equiv.) of chlorine gas generated by Graebes method.[20] After stirring (1 h), the original white suspension cleared to give a yellow solution. Chlorine gas was added for a further 1 h and stirring was continued for a further 2 h after this. The solution was then added to ice-cold water (1 l) and very vigorous effervescence of nitrogen took place. An oily material settled to the bottom of the vessel, the supernatent liquid was decanted off, and the remaining oily substance was distributed between ether (100 ml) and water (100 ml). The aqueous layer was further extracted with ether (3 × 100 ml) and the combined extracts were dried (Na_2SO_4) and evaporated to yield a reddish oil. This was distilled under reduced pressure to give 1,1,4-*trichloro*-4-*phenyl*-2,3-*diazabutadiene* (IV; Ar = Ph) (6·43 ml, 62%), a liquid, b.p. 162—164° at 1 mmHg (Found: C, 41·2; H, 2·2; Cl, 44·6; N, 11·95. $C_8H_5Cl_3N_2$ requires C, 40·7; H, 2·1; Cl, 45·2; N, 12·0%). The aqueous solution, after standing for a further 24 h, yielded a crystalline product, m.p. 108—110°. After two recrystallisations this material was identified (m.p. and i.r.) as benzoic acid (10%), m.p. 120—122° (Found: C, 68·9; H, 4·9; O, 26·1. Calc. for $C_7H_6O_2$: C, 68·85; H, 4·9; O, 26·2%). Concentration of the aqueous layer at 70° to 50 ml, followed by further extraction with ether, yielded further quantities of benzoic acid (total yield 25%). Evaporation of the aqueous layer (50 ml) at 70° to dryness yielded no other identifiable product.

Chlorination of the remaining 1,1,4-trichloro-4-(*p*-substituted phenyl)-2,3-diazabutadienes (IV) (see Table 3) followed a similar pattern. In some cases precipitation of the intermediate hydrazonyl chlorides [6] occurred but these compounds redissolved on further addition of chlorine and the remainder of the isolation was as above. Where the hydrazonyl chlorides did not precipitate they could be shown to be present in solution by addition of water at an early stage of the chlorination. The precipitated solids were recrystallised from benzene–chloroform. With the *p*-nitro-, -bromo-, and -chloro-phenyl compounds, the corresponding benzoic acids were isolated as above, in 32, 25, and 40% yields, respectively. With the *p*-tolyl and *p*-cumenyl compounds, the by-products were the corresponding *p*-substituted *m*-chlorobenzoic acids in 30 and 28% yields, respectively.

Chlorination of p-*Methoxybenzylidene*(*tetrazol*-5-*yl*)-*hydrazine* (VI; Ar = *p*-MeO·C_6H_4).—To a well-stirred, ice-cooled suspension of *p*-methoxybenzylidene(tetrazol-5-yl)-hydrazine (VI; Ar = *p*-MeO·C_6H_4) (10 g, 40 mmol) in aqueous acetic acid (500 ml, 90%) was added an excess of chlorine gas. Treatment of this mixture as above, followed by addition to water, gave a mixture, which was extracted with benzene. Evaporation gave 1,1,4-*trichloro*-4-(m-*chloro*-p-*methoxyphenyl*)-2,3-*diazabutadiene* (XVII) (40%), m.p. 53—55° [from light petroleum (b.p. 60—80°)] (Found: C, 35·6; H, 1·9; Cl, 47·6; N, 9·1. $C_9H_6Cl_4N_2O$ requires C, 36·0; H, 2·0; Cl, 47·3; N, 9·3%). The crystalline, benzene-insoluble solid gave, after recrystallisation (aqueous ethanol), a compound which was identified (mixed m.p. and i.r.) as *m*-chloro-*p*-anisic acid (10%), m.p. 212—214° (Found: C, 51·0; H, 3·7; Cl, 19·5; O, 25·65. Calc. for $C_8H_7ClO_3$: C, 51·5; H, 3·75; Cl, 19·0; O, 25·7%). The original aqueous filtrate was concentrated at 70° to 30 ml, to yield a further crop of *m*-chloro-*p*-anisic acid (total yield 45%).

4-*Aryl*-1,1,4-*trimorpholino*-2,3-*diazabutadienes* (XVIII).—Typically, to a solution of 1,1,4-trichloro-4-phenyl-2,3-diazabutadiene (IV; Ar = Ph) (0·67 ml, 3·36 mmol) in benzene (50 ml) was added a solution of morpholine (1·86 ml, 20 mmol) in the same solvent (5 ml), and the solution was heated to reflux. A white precipitate quickly formed and the heating was continued for a total of 5 h. The precipitate was filtered off and dried (818 mg, 98%), m.p. 176—178° (Found: C, 38·6; H, 8·1; Cl, 28·9; N, 11·6; O, 12·75. Calc. for $C_4H_{10}ClNO$: C, 38·9; H, 8·1; Cl, 28·7; N, 11·3; O, 12·95%). This did not depress the m.p. of a pure sample of morpholine hydrochloride, m.p. 179—180°. The benzene filtrate was evaporated (Büchi) at 35° to yield brownish white 1,1,4-*trimorpholino*-4-*phenyl*-2,3-*diazabutadiene* (XVIII; Ar = Ph) (90%), m.p. 127—128° [from light petroleum (b.p. 60—80°)] (Found: C, 61·8; H, 7·5; N, 18·3; O, 12·35. $C_{20}H_{29}N_5O_3$ requires C, 62·0; H, 7·5; N, 18·1; O, 12·4%). The remaining trimorpholinodiazabutadienes (XVIII) (see Table 4) were prepared similarly.

4-*Aryl*-1,1,4-*tribromo*-2,3-*diazabutadienes* (V) (*by* J. Donovan *and* T. M. Lambe).—Typically, *p*-nitro-*N*-(tetrazol-5-yl)benzohydrazonyl bromide (3·12 g, 10 mmol) was suspended in 60% aqueous acetic acid (60 ml) and

[19] M. Busch and P. Bauer, *Ber.*, 1900, **33**, 1058.
[20] C. Graebe, *Ber.*, 1902, **35**, 43.

bromine (3·2 g, 40 mmol) in glacial acetic acid (12 ml) was added dropwise with stirring. This suspension was stirred for 3 days. The solid was filtered off, washed with acetic acid and ether, and dried. Extraction of the solid with boiling ether gave 1,1,4-*tribromo*-4-(p-*nitrophenyl*)-2,3-*diazabutadiene* (V; Ar = *p*-NO_2·C_6H_4) (55%), m.p. 107° (Found: C, 23·6; H, 1·05; Br, 57·4; N, 10·3; O, 7·65. $C_8H_4Br_3N_3O_2$ requires C, 23·2; H, 0·95; Br, 57·95; N, 10·15; O, 7·75%). The analogous *p*-chloro- and *p*-bromo-substituted-compounds were similarly prepared: 1,1,4-*tribromo*-4-(p-*chlorophenyl*)-2,3-*diazabutadiene* (30%), m.p. 50—51° (Found: C, 24·0; H, 1·2; Br, 59·0; Cl, 8·7; N, 6·95. $C_8H_4Br_3ClN_2$ requires C, 23·8; H, 1·0; Br, 59·5; Cl, 8·8; N, 6·95%); 1,1,4-tribromo-4-(*p*-bromophenyl)-2,3-diazabutadiene (32%), m.p. 69—71° (Found: C, 21·8; H, 0·9; Br, 71·0; N, 6·25. $C_8H_4Br_4N_2$ requires C, 21·4; H, 0·9; Br, 71·4; N, 6·25%).

Kinetic Measurements.—Instruments. The reaction vessel was a water-jacketed 25-ml cell maintained at 20 ± 0·02 °C. The indicator system consisted of a platinum electrode [3 × 0·5 (i.d.) mm], rotated at 750 rev min^{-1} by a synchronous motor, and a saturated silver–silver chloride reference electrode, separated from the cell by a fine sintered-glass disc and an agar plug. The electrodes were connected to a Metrohm Polarecord E216R, which supplied the polarising voltage (+0·2 V) and recorded the diffusion current as a function of time. To generate the required quantities of bromine a Metrohm E211 coulometer was connected to a 5 cm platinum-gauze electrode as anode, and a silver cathode separated from the bromide solution in the reaction vessel by a sintered-glass disc and agar plug.

Solvents. Acetic acid was heated under reflux over chromium trioxide and distilled (b.p. 117—118°). Deionised water was distilled from potassium permanganate. The solvent for the reactions was made up by adding 70 ml of acetic acid to 30 ml of water and adding AnalaR potassium bromide (1·19 g, 0·01 mol).

Procedure. Aliquot portions (20 ml) of solvent were pipetted into the reaction vessel and equilibrated for 10 min. Bromine (1×10^{-2} mmol) was generated by passing a current of 10 mA through the solution for 193 s. The hydrazone (1 ml of $0·5 \times 10^{-2}$M-solution) was injected through a calibrated syringe, and the diffusion current (which under these conditions is proportional to the concentration of bromine in the reaction vessel) was recorded automatically as a function of time.

The reactions followed second-order kinetics reasonably well. The second-order rate constants were calculated according to the equation $k_2 = 2x/at(a - x)$ since each molecule of hydrazone reacted with 2 mol. equiv. of bromine [where a = initial concentration of bromine in mol l^{-1} = (quantity of bromine generated)/(volume of solvent) = ci (where c is a constant, and i is the current in amps), and $(a - x)$ = concentration of bromine in mol l^{-1} at $t = ci$ (where i is the current in amps at t s)]. The rate constants calculated in this way were found to rise gradually with time. The initial rate constants k_0 were obtained by plotting values of k against time and extrapolating to $t = 0$.

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