

Chemistry of Polyhalogenodiazabutadienes. Part V.¹ Routes to New Triazolyl Systems: Substituted 3-Amino-4,5-diazotriazoles

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Reaction of the 4-aryl-1,1,4-trichloro-2,3-diazabutadienes (III; X = Cl) with aniline formed the new 3-anilino-5-aryl-4-phenyl-1,2,4-triazoles (VIII). Treatment of the 1-aryl-1,4-dichloro-4-morpholinodiazabutadienes (X) with aniline gave both the 3-morpholino- (XII) and 3-anilino-triazoles (VIII), the latter being formed by amine displacement. The mechanism of formation of the anilino-triazole (VIII) from the trichloride (III; X = Cl) involved initial replacement of one of the geminal chlorine atoms in (III) followed by replacement of the second to form *N*-(*NN'*-diphenylamidino)-(*p*-substituted)benzohydrazonyl chlorides (VII; X = Cl), which then cyclised to form the triazoles (VIII) in high yields. The hydrazonyl bromides (VIII; X = Br) have been prepared and cyclised in triethylamine to give the anilino-triazoles (VIII), in almost quantitative yields.

As we have discussed¹ chlorine and bromine cleave the tetrazol-5-ylhydrazines (I) to yield either dihalogeno-(II) or trihalogeno-diazabutadienes (III) depending upon the conditions. The reaction of the dibromides (II; X = Br) with aniline to yield the carbanilohydrazide *N*-phenylimides (IV) established the positions of the two bromine atoms. With the trihalides (III; X = Cl) there was the possibility that reaction with primary amines could lead to triazoles by a sequential process such as outlined in Scheme 1. In this scheme

an intramolecular cyclisation [(VII) \rightarrow (VIII)] competes with intermolecular reaction to yield the amidinohydrazide imide (V). The present paper describes the reactions outlined in Scheme 1.²

RESULTS AND DISCUSSION

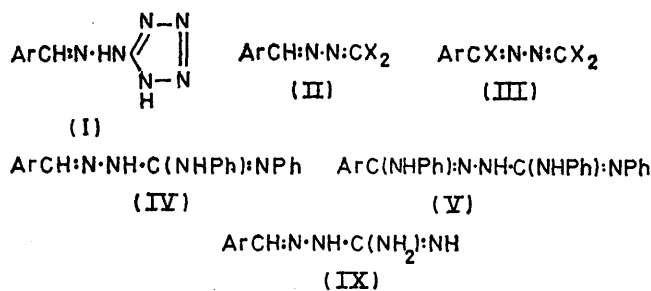
When an excess of aniline was added to 1,1,4-trichloro-4-*p*-nitrophenyl-2,3-diazabutadiene (III; Ar = *p*-NO₂·C₆H₄, X = Cl) a spontaneous and vigorously

¹ Part IV, J. K. O'Halloran, D. A. Cronin, J. Cronin, and F. L. Scott, preceding paper.

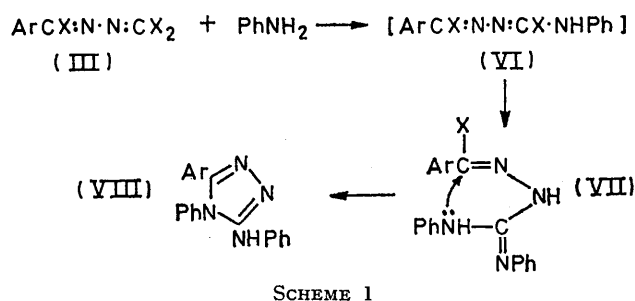
² Preliminary communication, J. K. O'Halloran and F. L. Scott, *Chem. Comm.*, 1971, 426.

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exothermic reaction took place with the deposition of a gummy solid. On leaching with dilute HCl (to remove any excess of aniline), this yielded the triazole (VIII);

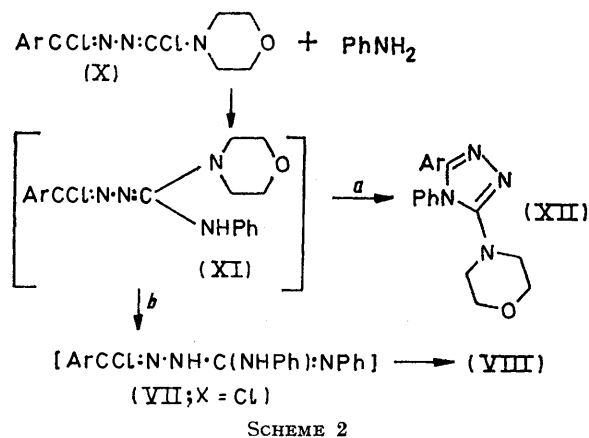


Ar = *p*-NO₂·C₆H₄) in excellent (>90%) yield. Similar reactions occurred with the corresponding *p*-bromo- and *p*-chloro-phenyl and *p*-cumenyl derivatives. The analytical data, molecular weights, and i.r. spectra of the products all confirm the 1,2,4-triazole structure.



SCHEME 1

Thus, all show C=N stretching absorption at 1605 (± 3) cm⁻¹, consistent with a similar absorption in the triazole ring.³ Similarly a group of three bands between 1300—1250 cm⁻¹, which appear in the i.r. spectra



SCHEME 2

of all these compounds, have been assigned to the C-N vibrations of the triazole ring.⁴

³ E. Lieber, D. R. Levering, and L. J. Patterson, *Analyst. Chem.*, 1951, **23**, 1594.

⁴ M. Dziewonska, *Spectrochim. Acta*, 1967, **23A**, 1195.

⁵ J. K. O'Halloran, J. A. Cronin, J. Donovan, and F. L. Scott, in preparation.

When treated with 2 mol. equiv. of a secondary amine such as morpholine,⁵ the trichlorides [*e.g.* (III; Ar = *p*-ClC₆H₄, X = Cl)] yielded the morpholino-compound (X; Ar = *p*-ClC₆H₄). When stirred with an excess of aniline, and treated as before, this gave a solid mixture, which was separated into the corresponding 3-anilino-5-*p*-chlorophenyl-4-phenyl-1,2,4-triazole (VIII; Ar = ClC₆H₄) (78%) and the analogous 3-morpholino-derivative (XII; Ar = *p*-ClC₆H₄) (20%) [the triazoles (XII) contained the sets of bands in the i.r. just described for materials (VIII) with essentially no shifts in position]. The triazoles (VIII) are formed by a transamination between aniline and morpholine [as in (XI) → (VII)]. Transaminations of this type are well known.⁶ That transamination occurred before and not after cyclisation was demonstrated by keeping a typical 3-morpholinotriazole (XII; Ar = *p*-NO₂·C₆H₄) in a ten-fold excess of aniline at 80° for 4 h, whereupon the starting morpholino-compound was recovered in >95% yield. The competition between aniline inducing both halogen replacement and cyclisation (process *a*), and causing the three-fold process (*b*) of transamination, halogen replacement, and cyclisation is surprisingly sensitive to the nature of the *p*-substituent in the aryl ring of the substrate: thus the ratio of morpholino- (XII) to anilino-triazole (VIII) varies from 1:3 for the *p*-nitro-substituted dichlorodiazabutadiene (X; Ar = *p*-NO₂·C₆H₄) to 1:20 for the corresponding *p*-isopropyl substituted compound (X; Ar = *p*-PrⁱC₆H₄).

We base the key mechanistic sequence (see Scheme 1) on the following facts. First, we have established⁵ that when a secondary amine reacts with a trihalogeno-diazabutadiene (III) it reacts preferentially (at least in an aprotic solvent) at the geminal halogen pair, selectively displacing one of these. Hence we feel that primary amines should do likewise: hence the step (III) → (VI). Secondly, we have shown that when aniline reacts with a dibromide (II; X = Br), it readily displaces both halogens to form an amidinohydrazide so that the postulation of the carbanilohydrazide *N*-phenylimide intermediate (VII) in this case is consistent.

We next attempted to confirm this sequence by synthesis of the key intermediates (VII). The appropriate *N*-(*p*-substituted benzylidene)carbanilohydrazide *N*-phenylimides (IV) were readily available by literature techniques.⁷ However despite the fact that we had been able to brominate smoothly the corresponding unsubstituted amidines [*i.e.* (IX)],⁸ bromination of compounds (IV) presented some difficulties. The reactions were not very reproducible and frequently proved impossible to stop at the monobromination stage, even when identical conditions were used in duplicate runs.

For example, when a solution of bromine in acetic

⁶ R. K. Bartlett and I. R. Humphrey, *J. Chem. Soc. (C)*, 1967, 1664; J. C. Martin, K. R. Barton, P. G. Gott, and R. H. Mean, *J. Org. Chem.*, 1966, **31**, 943.

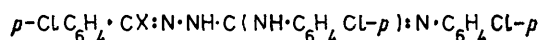
⁷ M. Busch and P. Bauer, *Ber.*, 1900, **33**, 1058.

⁸ F. L. Scott and T. A. F. O'Mahony, in preparation.

acid was added to a suspension of *p*-nitrobenzylidene-compound (IV; Ar = *p*-NO₂·C₆H₄) in acetic acid, work-up gave the hydrobromide of the *p*-nitrobenzohydrazonyl bromide [(VII), HBr; Ar = *p*-NO₂·C₆H₄, X = Br] (20%). Work-up of the acidic filtrate gave mixtures of compounds containing three, four, and even six bromine atoms. Exact repetition of the foregoing operations often only gave polybromo-compounds. Low yields of the hydrobromides of the hydrazonyl bromides (VII) were obtained from attempted bromination of the other compounds (IV): polybromination also occurred. The high reactivity of the *N*-phenyl groups in compounds (IV) towards attack by electrophiles is to be expected.⁹

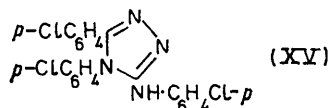
Despite the difficulties involved in their preparation, sufficient quantities of compounds (VII) were obtained to test their reactivity. When the *p*-nitro-compound [(VII), HBr; Ar = *p*-NO₂·C₆H₄] was treated with an excess of triethylamine in boiling benzene, work-up gave the 3-anilino-1,2,4-triazole (VIII; Ar = *p*-NO₂·C₆H₄) (94%). The remaining hydrazonyl bromides (VII) behaved similarly: these reactions all adding weight to our postulated step (VII) → (VIII). Comparable ring closures must have been involved in the formation of triazolones and triazoles from the reaction of carbanilohydrazide *N*-phenylimide with phosgene,¹⁰ thiophosgene,¹⁰ and *N*-dichloromethylenebenzamide,¹¹ but in these reactions any intermediary halogen compounds were not isolated.

To generalise this cyclisation [(VII) → (VIII)] to 1,2,4-triazoles (and to avoid the complications of polybromination) the deactivated *p*-chlorocarbanilohydrazide *N*-*p*-chlorophenylimide was prepared. Bromination (1 equiv. of bromine in glacial acetic acid) of its



(XIII) X = H

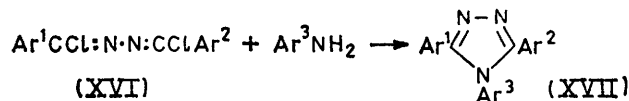
(XIV) X = Br



p-chlorobenzylidene derivative (XIII) proceeded smoothly yielding the hydrobromide of corresponding hydrazonyl bromide (XIV) in 80% yield. This was converted quantitatively into the corresponding triazole (XV) by heating under reflux in benzene containing an excess of triethylamine. This triazole (XV) was also prepared in high yield (92%) by reaction of *p*-chloroaniline with the trichloride (III; Ar = *p*-ClC₆H₄, X = Cl) in benzene.

The key reaction sequence in this present work has been that formulated in Scheme 1 with the trichloro-

diazabutadienes as substrates. There has been reported in the literature one other similar (but more limited) process, namely the reaction of primary amines with dichloroaldehyde azines or with 1,4-dichlorodiazabutadienes (see Scheme 3). Stolle¹² reported the first example of this reaction (with Ar¹ = Ar² = Ar³ = Ph), Klingsberg¹³ gave an additional example (Ar¹ =



SCHEME 3

Ph, Ar² = anthraquinolyl), and more recently some variations in the scheme involving Ar³ have been recorded.¹⁴ While these syntheses are more restricted than that reported herein, in that Ar¹ generally is identical with Ar², the approaches are complementary. The Stolle-type reactions in general also used much more forcing conditions than ours (Stolle describes his synthesis as needing temperatures just below the b.p. of aniline, *i.e.* 180°). We briefly examined his reaction further and found indeed that attempted reaction of the dichloroazine (XVI; Ar¹ = Ar² = Ph) in an excess of aniline either at room temperature or at 50° for 10 h only yielded starting material. However at 75° the diphenyl compound dissolved, a vigorous reaction soon began, and the temperature of the mixture rose to 140°. Work-up of the gummy solid which was deposited yielded the triazole (XVII; Ar¹ = Ar² = Ar³ = Ph) (95%). Stolle's materials, while not requiring the forcing conditions he recommended, are however less reactive than either the corresponding trichlorodiazabutadienes (III; X = Cl) or their mono-amino-derivatives (X).

EXPERIMENTAL

The general information is described in the preceding paper.¹

3-Anilino-5-aryl-4-phenyl-1,2,4-triazoles (VIII).—Typically, to 1,1,4-trichloro-4-(*p*-cumenyl)-2,3-diazabutadiene (III; Ar = *p*-PrⁱC₆H₄, X = Cl) (0.5 ml, 2.2 mmol) was added aniline (1.5 ml, 16.12 mmol). An immediate and vigorously exothermic reaction took place and a gummy solid was formed. This was stirred with hydrochloric acid (0.25N, 40 ml) for 30 min and then filtered. The insoluble material was washed with water (30 ml), filtered, and dried. One recrystallisation gave 3-anilino-5-(*p*-cumenyl)-4-phenyl-1,2,4-triazole (VIII; Ar = *p*-PrⁱC₆H₄) (94%), m.p. 200–202° (from ether) (Found: C, 77.7; H, 6.2; N, 15.55%; *M*, 355.21. C₂₃H₂₂N₄ requires C, 77.95; H, 6.2; N, 15.5%; *M*, 354.46). The remaining anilino-triazoles were prepared similarly (see Tables 1 and 2).

5-Aryl-3-morpholino-4-phenyl-1,2,4-triazoles (XII).—Typically to 1,4-dichloro-4-(*p*-chlorophenyl)-1-morpholino-2,3-diazabutadiene (X; Ar = *p*-ClC₆H₄) (1 g, 3.1 mmol) [prepared from compounds (III; X = Cl)⁵] was added

¹² R. Stolle, *J. prakt. Chem.*, 1906, **73**, 288.

¹³ E. Klingsberg, *J. Amer. Chem. Soc.*, 1958, **80**, 5786.

¹⁴ A.-G. Haco, Fr.P. M2723/1964 (*Chem. Abs.*, 1965, **62**, 11829C); B.P. 970,480/1964 (*Chem. Abs.*, 1965, **62**, 567d); J. Pauge and H. Tondys, *Dis. Pharm. Pharmacol.*, 1970, **22**, 217.

⁹ F. D. Chattaway and H. Irving, *J. Chem. Soc.*, 1935, 90; J. M. Burgess and M. S. Gibson, *Tetrahedron*, 1962, **18**, 1001.

¹⁰ M. Busch and Th. Ulwev, *Ber.*, 1902, **35**, 1716.

¹¹ H. Reimlinger, W. R. F. Lingier, and J. J. Vaudewalle, *Chem. Ber.*, 1971, **104**, 639.

aniline (1.5 ml, 16.12 mmol). The resulting suspension went into solution gradually and then (*ca.* 3 min) a very exothermic reaction took place and a solid formed. To this was added hydrochloric acid (0.25N, 20 ml) and the

TABLE 1

Products of the reactions of trichlorides (III; X = Cl) and dichlorides (X) with aniline, and of hydrazonyl bromides (VII; X = Br) with triethylamine

Y in Ar = <i>p</i> -YC ₆ H ₄	M.p. (°C) (VIII)	Yield (%)			M.p. (°C) (XII)	Yield (%) from (X)
		from (III)	from (X)	from (VII)		
Pr ^t	200—202	94	90	92	170—172	4
Cl	245—247	95	76	94	198—200	20
Br	242—244	89	78	94	195—197	20
NO ₂	255—256	90	75	92	189	23

mixture was stirred for 10 min. The insoluble material was filtered off, stirred in water (20 ml), refiltered, and dried. This material was extracted with ether (2 × 30 ml) and the insoluble material gave 3-anilino-5-*p*-chlorophenyl-4-phenyl-1,2,4-triazole (VIII; Ar = *p*-ClC₆H₄) (78%), m.p.

as it required heating at 75° to cause reaction. However, when it did react, the reaction was exothermic. The work-up was as for the *p*-chloro-substituted compound.

Hydrobromides of N-(NN'-Diphenylamidino)-(p-substituted)-benzohydrazonyl Bromides (VII; X = Br).—These reactions were not reproducible (see text) and led to variously-substituted bromides in different runs. The yields of the products (VII) were rarely >10% except in the case of the *p*-nitro-substituted compound where yields >20% were obtained on a number of occasions. Below is described a typical run.

To a solution of *N*-(*p*-bromobenzylidencarbanilohydrazide *N*-phenylimide⁷ (IV; Ar = *p*-BrC₆H₄) (2 g, 5.73 mmol) in glacial acetic acid (40 ml), a solution of bromide (0.3 ml, 5.73 mmol) in the same solvent (10 ml) was added dropwise during 2 h with stirring. The resulting suspension was stirred for a further 2 h and the insoluble material was filtered and dried. This material was recrystallised from acetic acid to give the hydrobromide of *p*-bromo-*N*-(*NN'*-diphenylamidino)benzohydrazonyl bromide (VII; Ar = *p*-BrC₆H₄) (20%), m.p. 208—209° (Found: C, 43.2; H, 3.1; Br, 43.6;

TABLE 2

Analytical data for the anilino-triazoles (VIII)

Y in Ar = YC ₆ H ₄	Formula	Found (%)				Required (%)			
		C	H	N		C	H	N	
Pr ^t	C ₂₃ H ₂₂ N ₄	77.7	6.2	15.55		77.95	6.2	15.5	
Cl	C ₂₀ H ₁₅ ClN ₄	69.3	4.05	16.1	10.5(Cl)	69.25	4.3	16.15	10.25(Cl)
Br	C ₂₀ H ₁₅ BrN ₄	61.05	3.5	14.55	20.95(Br)	61.4	3.85	14.3	20.45(Br)
NO ₂	C ₂₀ H ₁₅ N ₅ O ₂	67.15	4.15	19.85	8.9(O)	67.2	4.2	19.6	8.95(O)

TABLE 3

Analytical data for the morpholino-triazoles (XII)

Y in Ar = YC ₆ H ₄	Formula	Found (%)				Required (%)			
		C	H	N	O	C	H	N	O
Pr ^t	C ₂₁ H ₂₄ N ₄ O	72.5	6.75	15.9	4.85	72.4	6.9	16.1	4.6
Cl	C ₁₈ H ₁₇ ClN ₄ O	63.0	5.1	16.35	5.05	63.45	5.0	16.45	4.7
Br	C ₁₈ H ₁₇ BrN ₄ O	56.3	4.4	14.45	4.05	56.1	4.4	14.55	4.15
NO ₂	C ₁₈ H ₁₇ N ₅ O ₃	61.65	4.8	19.8	13.75	61.55	4.85	19.95	13.7

TABLE 4

Physical data for the hydrobromides of *N*-(*NN'*-diphenylamidino)-(p-substituted)benzohydrazonyl bromides (VII; X = Br)

Y in Ar = <i>p</i> -YC ₆ H ₄	M.p. (°C)	Yield (%)	Formula	Found (%)				Required (%)			
				C	H	Br	N	C	H	Br	N
Pr ^t	190—192	11	C ₂₃ H ₂₄ Br ₂ N ₄	53.7	4.7	30.5	11.1	53.5	4.65	31.0	10.85
Cl	200—202	22	C ₂₀ H ₁₇ Br ₂ ClN ₄	46.2	3.1	32.0	11.7	47.2	3.3	31.5	11.0
Br	208—209	20	C ₂₀ H ₁₇ Br ₃ N ₄	43.2	3.1	43.6	10.2	43.4	3.1	43.5	19.2
NO ₂	218—220	40	C ₂₀ H ₁₇ Br ₂ N ₅ O ₂	46.45	3.3	31.0	13.4	46.2	3.3	30.8	13.5

245—247° (from 95% ethanol) (Found: C, 69.5; H, 4.35; Cl, 9.95; N, 16.15. C₂₀H₁₅ClN₄ requires C, 69.25; H, 4.3; Cl, 10.25; N, 16.15%). The ether, upon evaporation, yielded 5-*p*-chlorophenyl-3-morpholino-4-phenyl-1,2,4-triazole (XII; Ar = *p*-ClC₆H₄) (20%), m.p. 198—200° [from ether-light petroleum (b.p. 60—80°)] (Found: C, 63.0; H, 5.1; N, 16.35; O, 5.05%; *M*, 340.02. C₁₈H₁₇ClN₄O requires C, 63.45; H, 5.0; N, 16.45; O, 4.5%; *M*, 340.815). The remaining morpholino-dichlorides (X) were treated similarly and the products were isolated the same way (see Tables 1 and 3). The treatment for the *p*-nitro-substituted compound was slightly exceptional

N, 10.2%; *M*, 552.65. C₂₀H₁₇Br₃N₄ requires C, 43.4; H, 3.1; Br, 43.4; N, 10.2%; *M*, 553.11). The acetic acid filtrate was evaporated in a stream of air to a few ml and the gummy material which separated was filtered and air-dried. When this was agitated in ether, a white powdery solid which was filtered and dried to give *p*-bromo-[*N*-(2-bromophenyl)-*N'*-(2,4-dibromophenyl)amidino]benzohydrazonyl bromide hydrobromide (the compound contained six bromine atoms and was tentatively given this structure) (40%), m.p. 215—216° (from acetic acid) (Found: C, 30.95; H, 2.0; Br, 60.45; N, 6.55. C₂₀H₁₄N₄Br₆ requires C, 30.35; H, 1.75; Br, 60.75; N, 7.1%). The acetic

acid filtrate contained a mixture of compounds whose analyses indicated the presence of many bromine atoms. The remaining substituted hydrazonyl bromide hydrobromides [(VII); HBr] (see Table 4) were also obtained in low yields.

3-Anilino-5-aryl-4-phenyl-1,2,4-triazoles (VIII) from *Hydrazonyl Bromides* (VII; X = BrHBr) and *Triethylamine in Benzene*.—Typically, to a suspension of the hydrobromide of the *p*-nitro-hydrazonyl bromide (VII; Ar = *p*-NO₂·C₆H₄, X = Br) (1 g, 1.92 mmol) in benzene (15 ml) was added a slight excess of triethylamine (freshly distilled) and the mixture was heated under reflux for 30 min. The insoluble material was filtered off, washed with water (3 × 10 ml), and dried to give a compound whose analysis and i.r. spectrum were identical with *3-anilino-5-p-nitrophenyl-4-phenyl-1,2,4-triazole* (VIII; Ar = *p*-NO₂·C₆H₄) and which did not depress the m.p. of an authentic sample [prepared from the trichloride (III; X = Cl, Ar = *p*-NO₂·C₆H₄)] of this material (92%), m.p. 254—255° (Found: C, 67.35; H, 4.2; N, 19.7; O, 8.7. C₂₀H₁₅N₅O₂ requires C, 67.2; H, 4.2; N, 19.6; O, 8.95%). Details of the yields and m.p.s of these triazoles are summarised in Table 1.

3-(p-Chloroanilino)-4,5-bis-(p-chlorophenyl)-1,2,4-triazole (XV).—To a solution of the *p*-chlorotrichloride (III; Ar = *p*-ClC₆H₄, X = Cl) (1 g, 3.7 mmol) in benzene (3 ml) was added a solution of *p*-chloroaniline (3.5 g, 22.2 mmol) in hot benzene (5 ml). After a few min, a vigorously exothermic reaction took place and a gummy solid formed. When this was treated as before with hydrochloric acid (0.25N, 30 ml) and water (30 ml), it yielded *3-(p-chloroanilino)-4,5-bis-(p-chlorophenyl)-1,2,4-triazole* (XV) (92%), m.p. 255—256° (from 95% ethanol) (Found: C, 57.9; H, 3.0; Cl, 25.7; N, 13.4. C₂₀H₁₂Cl₃N₄ requires C, 57.9; H, 2.9; Cl, 25.7; N, 13.5%).

p-Chloro-N-(p-chlorobenzylidene)carbanilohydrazide N-(p-Chlorophenyl)imide (XIII).—To a solution of *p*-chloro-carbanilohydrazide *N*-(*p*-chlorophenyl)imide⁷ (4.3 g, 14.6 mmol) in hot absolute ethanol (100 ml), was added a solution of *p*-chlorobenzaldehyde (2.0 g, 14.6 mmol) in the same solvent (20 ml). One drop of conc. nitric acid was added and the solution was warmed gently for 10 min and then cooled and agitated to give the *carbanilohydrazide imide* (XIII) (70%), m.p. 178—180° (from 95% ethanol) (Found: C, 57.35; H, 3.6; Cl, 25.65; N, 13.4. C₂₀H₁₅Cl₂N₄ requires C, 57.5; H, 3.6; Cl, 25.5; N, 13.4%). Further concentration of the ethanolic filtrate yielded a further crop of compound (XIII) (total yield 93%).

Hydrobromide of N-[NN'-Bis-(p-chlorophenyl)amidino]-p-chlorobenzohydrazonyl Bromide (XIV).—To a solution of the carbonilohydrazide imide (XIII) (1 g, 2.4 mmol) in acetic acid (25 ml) was added dropwise with constant stirring a solution of bromine (0.24 ml, 4.8 mmol) in the same solvent (10 ml). On the addition of the first few

drops of bromine, the solution turned black but on stirring for 3 h a red suspension was obtained. This was filtered off and washed with ether to give the *hydrobromide* of the *hydrazonyl bromide* (XIV) (65%), m.p. 218—219° (from acetic acid) (Found: C, 41.35; H, 2.6; Br, 28.0; Cl, 18.05; N, 10.0. C₂₀H₁₅Br₂Cl₂N₄ requires C, 41.55; H, 2.6; Br, 27.7; Cl, 18.45; N, 9.7%).

3-(p-Chloroanilino)-4,5-bis-(p-chlorophenyl)-1,2,4-triazole (XV) from the *Hydrazonyl Bromide Hydrobromide* (XIV); HBr.—To a suspension of the hydrazonyl bromide hydrobromide (XIV), HBr (200 mg, 0.47 mmol) in benzene (10 ml) was added triethylamine (20 ml). The resulting suspension was heated under reflux for 15 min and then the insoluble material was filtered off and dried. This was then stirred in water (20 ml) for 5 min and the insoluble material was filtered off, dried, and recrystallised (95% ethanol) to give a compound whose analysis and i.r. spectrum were identical with a sample of the triazole prepared from trichloride (III; Ar = *p*-ClC₆H₄, X = Cl) (92%), m.p. 253—254° (Found: C, 57.75; H, 2.9; Cl, 25.8; N, 13.55%).

3,4,5-Triphenyl-1,2,4-triazole (XVII; Ar¹ = Ar² = Ar³ = Ph) from *1,4-Dichloro-1,4-diphenyl-2,3-diazabutadiene* (XVI; Ar¹ = Ar² = Ph).—Aniline (1.5 ml, 16.12 mmol) was added to *1,4-dichloro-1,4-diphenyl-2,3-diazabutadiene*¹² (XVI; Ar¹ = Ar² = Ph) (1 g, 3.6 mmol). After 10 h at room temperature no reaction took place and only starting material was recovered on work-up of the suspension. The same result was obtained after 10 h at 50° so the mixture was suspended in a bath at 75°. The suspension slowly dissolved whereupon a vigorous, exothermic reaction took place, with the temperature rising quickly to 150° to form a gummy solid, which, when treated with hydrochloric acid (0.25N) and water, as before, gave *3,4,5-triphenyl-1,2,4-triazole* (XVII; Ar¹ = Ar² = Ar³ = Ph) (95%), m.p. 290—292° (from 95% ethanol) (lit.,¹² 292°) (Found: C, 80.6; H, 5.05; N, 14.35. Calc. for C₂₀H₁₅N₃: C, 80.8; H, 5.05; N, 14.15%).

Reaction of Aniline with 3-Morpholino-5-p-nitrophenyl-4-phenyl-1,2,4-triazole (XII; Ar = *p*-NO₂·C₆H₄).—A solution of compound (XII; Ar = *p*-NO₂·C₆H₄) (500 mg, 1.4 mmol) in a ten-fold excess of aniline (3 ml) was warmed at 75° for 8 h and then cooled. The solution was shaken with dry ether (30 ml) and a material precipitated out which after filtration, drying, and recrystallisation (benzene) gave a compound whose analysis, i.r., and m.p. were identical with starting material (95%). No trace of any anilino-triazole (VIII; Ar = *p*-NO₂·C₆H₄) was detected in a very careful work-up, involving t.l.c. treatment of the solution.

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