Triazines and Related Products. Part XIII.[1] Decomposition of 4-Arylamino-1,2,3-benzotriazines and their Precursors in Secondary Amines

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4-Arylamino-1,2,3-benzotriazines (1) decompose in piperidine and related secondary amines to afford *NNN'*-trisubstituted 2-aminobenzamidines (4) in excellent yields. 4-*o*-Aminoanilinobenzotriazine (1f) yields 2-(2-aminophenyl)benzimidazole (9) when heated in ethylene glycol or piperidine. Nucleophilic attack by the amines at C-4 of the triazine ring is implicated in these transformations. 1-*o*-Cyanophenyl-3-*m*-cyanophenyltriazene (13a) is unreactive in piperidine whereas the *p*-cyanophenyltriazene isomer (13b) yields 2-amino-*N'*-*p*-cyanophenyl-*NN*-pentamethylenebenzamidine (4b). 1,3-Bis-*o*-cyanophenyltriazene (13c) rearranges and decomposes in boiling piperidine, pyrrolidine, morpholine, diethylamine, di-n-propylamine, and piperazine to afford the triazenylquinazolines (19)—(24), respectively.

THE ease with which the diazo-fragment of 1,2,3-benzotriazines is replaced in both heterolytic and homolytic processes makes these compounds versatile intermediates in the synthesis of *ortho*-disubstituted arenes.[2-4] This reactivity is exemplified by the behaviour of 3,4-dihydro-4-imino-1,2,3-benzotriazines and the related benzotriazin-4(3*H*)-ones in boiling secondary amines where the attacking nucleophile initiates heterolytic ring cleavage at different sites in the benzotriazine substrate.[1] With substituted 4-amino-1,2,3-benzotriazines now available by an improved process,[5] it was of interest to examine their behaviour towards secondary amines.

4-Anilinobenzotriazine (1a) dissolved in boiling piperidine with concomitant evolution of nitrogen to afford a cream-coloured base. Analytical and spectral data, together with the detection of a diazotisable amino-group established that this product was 2-amino-*N'*-phenyl-*NN*-pentamethylenebenzamidine (4a) rather than the isomeric amidine (5a). With the exception of the *o*-aminoanilinotriazine (1f) (see later) all the 4-arylaminotriazines (1a—i) also formed the appropriate benzamidines (4) in boiling piperidine. As expected, pyrrolidine or morpholine also successfully served as the base component in some cases. All the amidines had diazotisable amino-groups, and one such amidine (4b) was preparatively converted into an azonaphthol derivative which had analytical and spectroscopic characteristics appropriate to structure (6b). Yields of amidines were excellent (80—90%) but the aralkylaminobenzotriazines (1j and k) were recovered unchanged from boiling piperidine or morpholine.

[1] Part XII, M. S. S. Siddiqui and M. F. G. Stevens, preceding paper.

[2] J. G. Erickson, 'The 1,2,3-Triazines,' in 'The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, Interscience, New York, 1956, vol. 10.

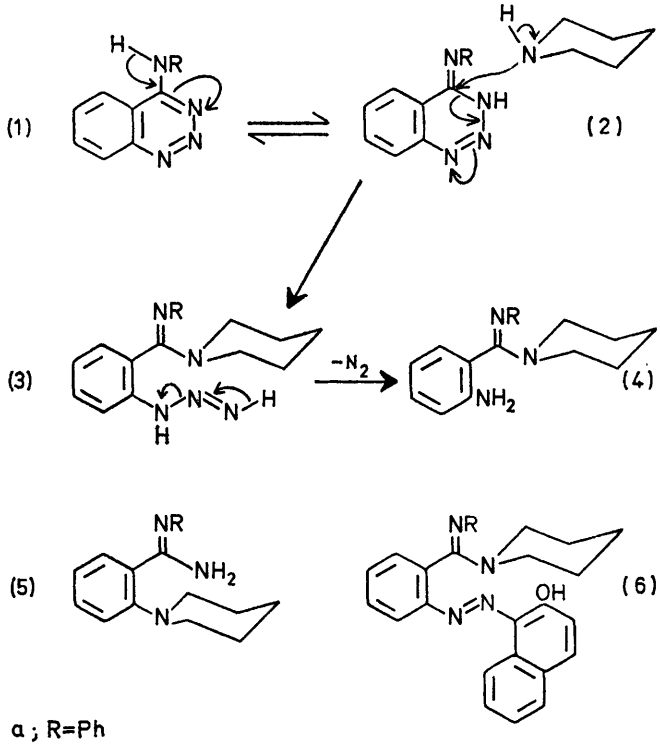
[3] S. M. Mackenzie and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1970, 2298.

[4] A. C. Mair and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1971, 2317.

[5] Part XI, M. S. S. Siddiqui and M. F. G. Stevens, *J.C.S. Perkin I*, 1973, 609.

In one instance [the reaction between 4-*p*-cyanoanilinobenzotriazine (1b) and morpholine] a deep yellow, high-melting solid was obtained in addition to the expected amidine. The structure of this substantial by-product will be discussed in a future paper.

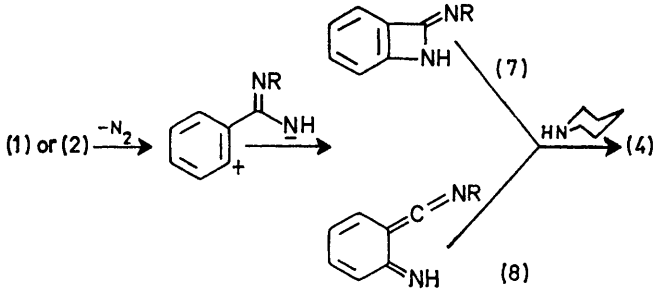
Most probably, the piperidine attacks C-4 of the arylimino-tautomers (2) of the triazines. This leads to unstable acyclic triazenes (3) which lose nitrogen either heterolytically (as depicted in Scheme 1), or possibly homolytically to afford the amidines (4). Similar mechanisms have been advanced to explain the formation of anthranilamides in the decomposition of benzotriazin-4(3*H*)-ones in either piperidine and its heteroalicyclic analogues,[1] or in high-boiling primary amines.[6] Alternatively (but less likely because of the low temperature involved), the amidines could arise by reaction of piperidine with either a benzazet-2(1*H*)-imine (7) or its valence tautomer (8) formed by thermal extrusion of nitrogen from the starting benzotriazines (Scheme 2).



a ; R=Ph
b ; R=*p*-CN·C$_6$H$_4$
c ; R=*o*-NO$_2$·C$_6$H$_4$
d ; R=*m*-NO$_2$·C$_6$H$_4$
e ; R=*p*-NO$_2$·C$_6$H$_4$
f ; R=*o*-NH$_2$·C$_6$H$_4$
g ; R=*m*-NH$_2$C$_6$H$_4$
h ; R=*p*-NH$_2$·C$_6$H$_4$
i ; R=*p*-MeC$_6$H$_4$
j ; R=PhCH$_2$
k ; R=Ph[CH$_2$]$_2$

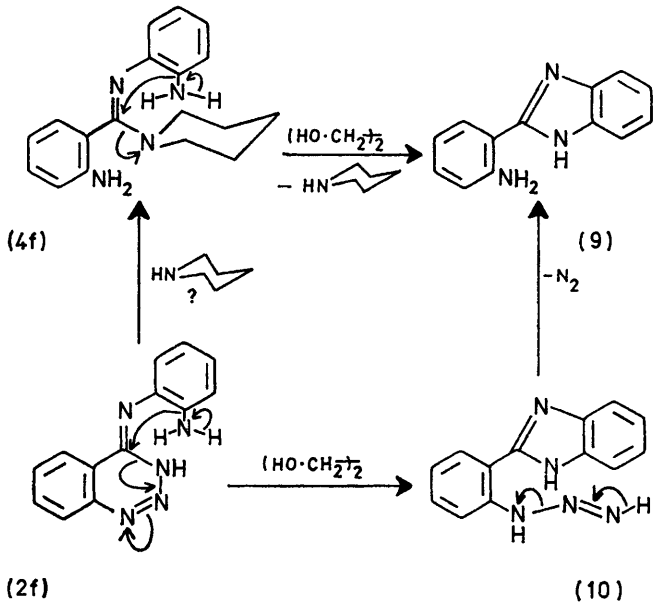
SCHEME 1

Catalytic hydrogenation of the nitro-amidines (4c—e) afforded the corresponding amines (4f—h), but the *o*-amino-derivative (4f) readily cyclised to 2-(2-aminophenyl)benzimidazole (9) in polar solvents (Scheme 3). This transformation provides incontrovertible support for structures (4) rather than (5) for the amidines.



SCHEME 2

4-*o*-Aminoanilinobenzotriazine [written as the arylimino-tautomer (2f)] also yields the benzimidazole (9) in boiling piperidine, but in this case the amidine (4f) is probably not an intermediate since the triazine (2f) in boiling ethylene glycol is itself quantitatively converted into the benzimidazole (9). In this latter



SCHEME 3

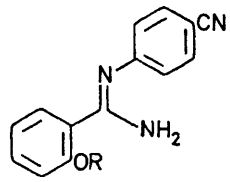
case the aminophenyl substituent of the triazine (2f) is favourably aligned for intramolecular attack at C-4 leading to the benzimidazole *via* an unstable triazene (10); but here again, the slight possibility that the reaction might involve a benzazetimine (or its tautomer) must be conceded.

In an earlier paper,[7] the reaction between 4-*p*-cyanoanilinobenzotriazine (1b) and high-boiling alcohols containing 1% potassium hydroxide was described.

[6] A. W. Murray and K. Vaughan, *J. Chem. Soc.* (*C*), 1970, 2070.

[7] S. M. Mackenzie and M. F. G. Stevens, *J.C.S. Perkin I*, 1972, 295.

The products, originally formulated as the ethers (11a—c) on the basis of their spectroscopic properties, are now known to contain diazotisable amino-groups and should be reformulated as imidates (12a—c). However, unlike other imidates, which react with amines to form amidines (Pinner synthesis),[8,9] the imidate (12a) does not undergo displacement of 2-methoxyethanol in boiling morpholine. The *NN*-pentamethyleneamidine (4b) was similarly stable in morpholine.



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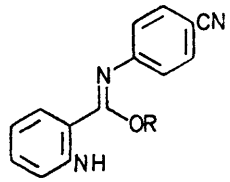


(12)

a; R = $[CH_2]_2$·OMe.

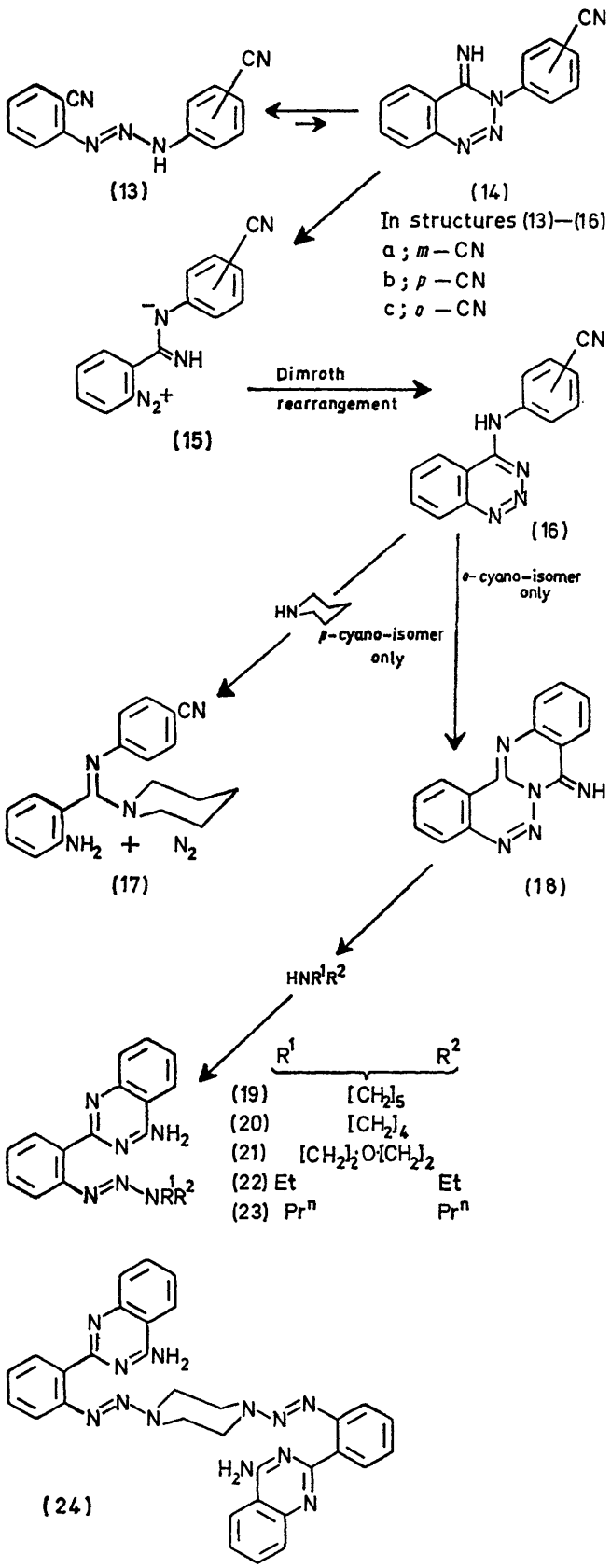
b; R = $[CH_2]_2$·OEt

c; R = $[CH_2]_3$Me

1-Aryl-3-*o*-cyanophenyltriazenes are starting materials for the synthesis of 4-arylaminobenzotriazines,[10] and the behaviour of the isomeric *o*-cyanophenyltriazenes (13a—c) towards piperidine and its analogues neatly illustrates the multiple roles of the nucleophiles as catalysts and reactants (Scheme 4). Although at low concentration piperidine catalyses the cyclisation (13a) ⟶ (14a),[10] when the triazene (13a) is boiled in excess of piperidine (1 h) an equilibrium, (13a) ⇌ (14a), is established. As the position of equilibrium overwhelmingly favours the acyclic form,[1] the triazene (13a) can be recovered nearly quantitatively.

1-*o*-Cyanophenyl-3-*p*-cyanophenyltriazene (13b) behaves differently. The influence of the powerful electron-attracting *p*-cyano-substituent in the imine (14b)[5,11] counters the tendency for this imine to revert to starting triazene by encouraging the competing Dimroth rearrangement (14b) ⟶ (15b) ⟶ (16b). The 4-*p*-cyanoanilinobenzotriazine (16b) thus formed then reacts with piperidine to afford the amidine (17), albeit in lower yield than in the corresponding reaction starting from preformed benzotriazine [designated (1b) in Scheme 1].

The reaction of 1,3-bis-*o*-cyanophenyltriazene (13c) with secondary bases is yet more complicated since both cyano-groups participate in covalency changes. This triazene in boiling piperidine, morpholine, pyrrolidine, diethylamine, or di-n-propylamine, with or without benzene as solvent, affords the triazenylquinazolines (19)—(23) in excellent yields; with piperazine the



SCHEME 4

[8] R. Roger and D. G. Neilson, *Chem. Rev.*, 1961, **61**, 179.
[9] R. L. Shriner and F. W. Neumann, *Chem. Rev.*, 1944, **35**, 351.
[10] H. N. E. Stevens and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1970, 765.
[11] D. J. Brown, 'Mechanisms of Molecular Migrations,' ed. Thyagarajan, vol. 1, p. 209.

product is the bis-quinazoline (24). In these cases the 4-*o*-cyanoanilinobenzotriazine (16c) formed as an intermediate is not diverted to amidines by the bases. Instead it cyclises to the tetracyclic triazine (18),[10] which then suffers ring-opening by the bases at N-2 (Scheme 4). In agreement, a sample of the tetracyclic triazine (18) independently prepared by diazotisation of 4-amino-2-(2-aminophenyl)quinazoline [12] also yielded the triazenes (19)—(21) in the appropriate boiling amines. This behaviour is to be expected of a polycyclic 1,2,3-triazine where both N-3 and C-4 of the triazine ring occupy bridgehead positions.[1]

The properties of the triazenes (19)—(24) fully support their assigned structures. All the compounds gave red colours when heated with 2-naphthol in acetic acid

The 60 MHz n.m.r. spectrum of the *NN*-pentamethylenetriazene (19) in $CDCl_3$ shows an aromatic multiplet (τ 2·1—2·9) and a signal for methylene protons split into two broad singlets at τ 6·5 and 8·52; the aromatic and aliphatic proton signals integrate correctly in a 4 : 5 ratio. In addition, the spectrum shows exchangeable amino- and water (of crystallisation) protons at τ 3·4 and 7·6, respectively.

The mass spectra of the triazenylquinazolines (19)—(23) are similar to those of related triazenyl-*s*-triazines in that the molecular ions are either very weak or absent.[1] The spectra all show abundant ions at *m/e* 221 ($C_{14}H_{11}N_3$) and 220 ($C_{14}H_{10}N_3$). The radical ion at *m/e* 221 is formed by loss of the triazene side-chain accompanied by H-rearrangement. The ion at *m/e*

Electronic absorption spectra ($\lambda_{max.}$/nm; log ε in parentheses) of 4-amino-2-arylquinazolines (in 95% ethanol)

Compound					
(19)†	236 (4·47)	289 (4·28)	317* (4·24)	329* (4·15)	348* (3·77)
(20)†	235 (4·40)	287 (4·20)	315 (4·18)	330* (4·09)	348* (3·74)
(21)	235 (4·61)	290 (4·33)	317* (4·16)	331* (4·04)	348* (3·66)
(22)‡	235 (4·45)	287 (4·22)	317* (4·18)	330* (4·10)	347* (3·72)
(23)	234 (4·39)	289 (4·19)	315 (4·17)	330* (4·09)	348* (3·68)
(24)	235 (4·68)	292 (4·42)	317* (4·39)	332* (4·29)	350* (3·94)
4-Amino-2-phenylquinazoline	254 (4·56)	285* (3·96)	304 (4·05)	321* (3·97)	333* (3·75)
4-Amino-2-(2-aminophenyl)quinazoline	240 (4·36)	265* (4·14)	303 (3·89)	337* (3·76)	360* (3·45)
4-Amino-2-(2-hydrazinophenyl)quinazoline	238 (4·55)	268* (4·21)	300 (4·02)	335* (3·88)	364* (3·77)

* Inflection. † With water of crystallisation. ‡ With benzene of crystallisation.

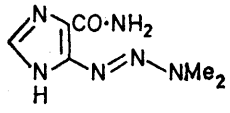
thus confirming the presence of an intact NNN-residue. The electronic absorption spectra differ significantly from those of related diaryltriazenes [10] in that the intense long-wavelength maximum characteristically centred at 360—380 nm in the spectra of the latter triazenes is absent: instead, the spectra closely resemble those of other 4-amino-2-arylquinazolines (Table), with a long-wavelength absorption showing considerable fine structure.

Solvation by both polar and non-polar solvents seems to be a general phenomenon in quinazolines,[12] and the triazenylquinazoline series is no exception. Both the piperidino- and pyrrolidino-derivatives (19) and (20) crystallised from aqueous polar solvents with one molecule of water of crystallisation, and this water was tenaciously held even if the hydrates were vacuum-dried or subsequently recrystallised from non-polar solvents. The solid-phase i.r. spectra of these triazenes showed strong, sharp absorptions at 3605 and 3615 cm^{-1}, respectively, attributable to an unassociated O–H stretching vibration; in the solution spectrum (CCl_4) of the triazene (19) this absorption occurs at 3500 cm^{-1} and is uninfluenced on dilution. Possibly the water molecules are trapped between the two bulky *ortho*-substituents, and these steric features prohibit intermolecular H-bonding. In contrast, the diethyltriazene (22) forms a benzene solvate, but in this case the solvent molecules are less firmly held; the compound melts and resolidifies to afford the desolvated form at 90°.

[12] M. W. Partridge and M. F. G. Stevens, *J. Chem. Soc.*, 1964, 3663.

220 arises either from the radical ion by H-atom loss, or alternatively by fission of the entire triazene fragment.

Finally, the triazenylquinazolines are structurally related to the alkylating agent 5-(3,3-dimethyltriazen-1-yl)imidazole-4-carboxamide (25), which has evoked



(25)

wide interest as a tumour-inhibitory agent.[13] Preliminary results indicate that the triazenylquinazolines (19)—(24) also exhibit cytotoxicity against human epidermoid carcinoma of the nasopharynx in cell culture.

EXPERIMENTAL

2-Amino-N′-phenyl-NN-pentamethylenebenzamidine (4a). —Nitrogen was evolved when 4-anilino-1,2,3-benzotriazine (3 g) [5] was boiled in piperidine (5 h). The brown solution was diluted with water and extracted with toluene. The combined extracts were dried ($NaSO_4$) and chromatographed on an alumina column. A mobile yellow band was eluted. The residue left when this fraction was evaporated was dissolved in 2N-hydrochloric acid, and the mixture was basified with concentrated aqueous ammonia. The precipitated *benzamidine* (2·7 g) crystallised from light petroleum (b.p. 60—80°) as cream rosettes, m.p. 97—98°

[13] Y. F. Shealy, *J. Pharm. Sci.*, 1970, **59**, 1533, and references therein; A. H. Gerulath and Ti Li Loo, *Biochem. Pharmacol.*, 1972, **21**, 2335.

(Found: C, 77·2; H, 7·8; N, 15·3. $C_{18}H_{21}N_3$ requires C, 77·4; H, 7·6; N, 15·0%).

2-*Amino*-N′-p-*cyanophenyl*-NN-*oxydiethylenebenzamidine*.—A solution of 4-*p*-cyanoanilinobenzotriazine (2·4 g) [5] in morpholine (40 ml) was boiled for 7 h, then kept at 0° for 7 days. The yellow solid which was collected (0·6 g) melted at 246—248° (efferv.); its structure will be discussed in a future paper. The remaining solution was diluted with water and extracted with toluene. Chromatography as above yielded the *benzamidine* (1·8 g), which crystallised from benzene–light petroleum as cream prisms, m.p. 117—118° (Found: C, 70·8; H, 5·8; N, 18·1. $C_{18}H_{18}N_4O$ requires C, 70·6; H, 5·9; N, 18·3%).

Similarly prepared were the following *benzamidine* derivatives: 2-*amino*-N′-*phenyl*-NN-*tetramethylene* (90%), m.p. 116—117° (yellow prisms from light petroleum) (Found: C, 76·9; H, 7·4; N, 15·6. $C_{18}H_{19}N_3$ requires C, 77·0; H, 7·2; N, 15·8%); 2-*amino*-NN-*oxydiethylene*-N′-*phenyl*- (85%), m.p. 124—125° (yellow rosettes from light petroleum) (Found: C, 72·5; H, 6·6; N, 15·0. $C_{17}H_{19}N_3O$ requires C, 72·6; H, 6·8; N, 14·9%); 2-*amino*-N′-p-*cyanophenyl*-NN-*pentamethylene* (88%), m.p. 118—119° (cream prisms from toluene–light petroleum) (Found: C, 74·9; H, 6·6; N, 18·4. $C_{19}H_{20}N_4$ requires C, 75·0; H, 6·6; N, 18·4%); 2-*amino*-N′-o-*nitrophenyl*-NN-*pentamethylene* (82%), m.p. 127—128° (yellow rods from ethanol) (Found: C, 66·3; H, 5·9; N, 16·9. $C_{18}H_{20}N_4O_2$ requires C, 66·7; H, 6·2; N, 17·3%); 2-*Amino*-N′-m-*nitrophenyl*-NN-*pentamethylene* (80%), m.p. 118—119° (yellow prisms from aqueous ethanol) (Found: C, 67·1; H, 6·1; N, 17·0%); 2-*amino*-N′-p-*nitrophenyl*-NN-*pentamethylene* (90%), m.p. 66—67° (yellow flakes from benzene–light petroleum) (Found: C, 66·7; H, 6·1; N, 16·8%); 2-*amino*-N′-m-*aminophenyl*-NN-*pentamethylene* (82%), m.p. 116—117° (cream rosettes from benzene–light petroleum) (Found: C, 73·8; H, 7·4; N, 18·9. $C_{18}H_{22}N_4$ requires C, 73·4; H, 7·5; N, 19·0%); 2-*amino*-N′-p-*aminophenyl*-NN-*pentamethylene* (80%), m.p. 173—174° (brown prisms from benzene–light petroleum) (Found: C, 73·3; H, 7·6; N, 19·0%); 2-*amino*-NN-*pentamethylene*-N′-p-*tolyl* (85%), m.p. 130—131° (yellow prisms from aqueous ethanol) (Found: C, 77·4; H, 7·6; N, 13·9. $C_{19}H_{23}N_3$ requires C, 77·8; H, 7·9; N, 14·3%).

2-*Amino*-N-o-*aminophenyl*-NN-*pentamethylenebenzamidine* (4f).—Catalytic hydrogenation of 2-amino-*N*-*o*-nitrophenyl-*NN*-pentamethylenebenzamidine (2·5 g) over palladium–charcoal (0·1 g) in ethanol (25 ml) (uptake 3 mol. equiv.) afforded the *diaminobenzamidine* (1·8 g), which crystallised from benzene–light petroleum as buff prisms, m.p. 95—96° (Found: C, 73·5; H, 7·6; N, 19·0%).

Catalytic hydrogenation of the *m*-nitro- (4d) and *p*-nitro- (4e) analogues afforded the diaminobenzamidines (4 g and h) (80 and 88%, respectively).

2-(2-*Aminophenyl*)*benzimidazole* (9).—(i) 4-*o*-Aminoanilino-1,2,3-benzotriazine (0·3 g) [10] was boiled in piperidine (2 ml) for 6 h. The brown solution, diluted with water, deposited a grey solid (0·25 g) which was identical (i.r. and m.p.)[14] with an authentic sample of the benzimidazole (9).

(ii) 4-*o*-Aminoanilinobenzotriazine (0·5 g) was boiled in ethylene glycol (5 ml) for 10 min. The diluted solution deposited the benzimidazole (0·4 g), identical with the foregoing sample.

[14] H. N. E. Stevens and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1970, 2308.

(iii) 2-Amino-*N*′-*o*-aminophenyl-*NN*-pentamethylenebenzamidine in boiling ethylene glycol formed the benzimidazole (85%) during 10 min.

N′-p-*Cyanophenyl*-2-(2-*hydroxy*-1-*naphthylazo*)-NN-*pentamethylenebenzamidine* (6b).—A solution of 2-amino-*N*′-*p*-cyanophenyl-*NN*-pentamethylenebenzamidine (0·77 g) in 2N-hydrochloric acid (10 ml) was diazotised with sodium nitrite (0·16 g) at 0°, and the resultant diazonium solution was coupled with 2-naphthol (0·29 g) in alkaline solution. The precipitated *naphthylazobenzamidine* (0·7 g) crystallised from ethanol as red needles, m.p. 204—205° (Found: C, 75·8; H, 5·8; N, 15·0. $C_{29}H_{25}N_5O$ requires C, 75·7; H, 5·5; N, 15·3%).

Decomposition of 1-o-*Cyanophenyl*-3-p-*cyanophenyltriazene*.—The triazene (2·0 g) [10] in piperidine (10 ml) was boiled (6 h) and the mixture was diluted with water. The precipitated gum slowly solidified, and crystallised from toluene–light petroleum to afford 2-amino-*N*-*p*-cyanophenyl-*NN*-pentamethylenebenzamidine (0·9 g), identical (m.p. and i.r.) with the sample prepared from 4-*p*-cyanoanilinobenzotriazine and piperidine.

When 1-*o*-cyanophenyl-3-*m*-cyanophenyltriazene (1·0 g) was boiled in piperidine (1 h) there was no change in u.v.–visible spectral characteristics. The yellow solution was poured into an excess of iced N-hydrochloric acid and extracted with ether. The evaporated extract afforded the starting triazene (0·95 g).

4-*Amino*-2-[2-(*piperidin*-1-*ylazo*)*phenyl*]*quinazoline* (19).—(i) 1,3-Bis-*o*-cyanophenyltriazene (2 g) was boiled in piperidine (5 ml) for 2 h. Dilution of the solution with water afforded a grey solid (2·2 g) which crystallised from acetone as buff prisms, m.p. 179—180° (efferv.) of the *piperidinylazophenylquinazoline hydrate* (Found: C, 64·9; H, 6·4; N, 23·9. $C_{19}H_{20}N_6,H_2O$ requires C, 65·1; H, 6·3; N, 24·0%).

(ii) 1,3-Bis-*o*-cyanophenyltriazene (1·0 g) in anhydrous benzene (20 ml) containing piperidine (0·5 ml) was boiled (5 h); the solution changed colour from red to pale brown. The gum left after removal of benzene did not crystallise until it was triturated with water; the product (1·1 g) was identical with the foregoing sample.

(iii) Quinazolino[3,2-*c*][1,2,3]benzotriazin-8(7*H*)-imine (18) (0·5 g),[12] boiled in piperidine (3 ml) for 1 h, afforded the same hydrate (0·55 g) when the cooled solution was diluted with water.

4-*Amino*-2-[2-(*morpholin*-4-*ylazo*)*phenyl*]*quinazoline* (21).—This *quinazoline* was prepared by boiling either 1,3-bis-*o*-cyanophenyltriazene (94% yield) or quinazolino[3,2-*c*]-[1,2,3]benzotriazin-8(7*H*)-imine (90% yield) in morpholine for 2 h, and diluting the solution with water. The product crystallised from acetone as buff prisms, m.p. 175—177° (efferv.) which were not solvated (Found: C, 64·3; H, 5·5; N, 25·2. $C_{18}H_{18}N_6O$ requires C, 64·7; H, 5·4; N, 25·2%); $\nu_{max.}$ (KBr) 3485, 3300, and 3150 (NH), 2960 and 2840 (aliphatic CH), and 1638 cm^{-1} (C=N), τ($CDCl_3$) 2·1—2·8 (m, aromatic CH), 3·6br (s, NH_2), and 6·4 (s, aliphatic CH).

4-*Amino*-2-[2-(*pyrrolidin*-1-*ylazo*)*phenyl*]*quinazoline* (20).—(i) Similarly prepared from 1,3-bis-*o*-cyanophenyltriazene in boiling pyrrolidine or in benzene containing pyrrolidine (2 mol. equiv.), the *pyrrolidinylazophenylquinazoline hydrate* (95 and 87% yield, respectively) crystallised from aqueous methanol as brown rosettes, m.p. 136—137° (efferv.) (Found: C, 64·7; H, 6·2; N, 24·8. $C_{18}H_{18}N_6,H_2O$ requires C, 64·3; H, 5·9; N, 25·0%).

(ii) From quinazolino[3,2-*c*][1,2,3]benzotriazin-8(7*H*)-imine (1·0 g) and boiling pyrrolidine (5 ml), the same quinazoline hydrate (1·2 g) was obtained when the solution was triturated with water.

4-Amino-2-[2-(3,3-diethyltriazen-1-yl)phenyl]quinazoline (22).—(i) A red-brown oil was formed when 1,3-bis-*o*-cyanophenyltriazene (2 g) was boiled in diethylamine (10 ml) for 2 h and the solution was diluted with water. The i.r. spectrum (KBr) showed $\nu_{max.}$ 3465, 3300, and 3100 cm^{-1} (NH). When the oil was mixed with benzene rapid crystallisation occurred and the NH stretching region of the i.r. spectrum was significantly changed ($\nu_{max.}$ 3315 and 3180 cm^{-1}). This product (1·7 g) crystallised from benzene as buff needles, m.p. 90° [with resolidification, finally melting at 142—143° (efferv.)] of the *diethyltriazenylphenylquinazoline benzene solvate* (Found: C, 71·9; H, 6·3; N, 21·0. $C_{18}H_{20}N_6,C_6H_6$ requires C, 72·3; H, 6·6; N, 21·1%).

(ii) When 1,3-bis-*o*-cyanophenyltriazene (2 g) was boiled in anhydrous benzene (40 ml) containing diethylamine (2 ml) for 8 h, the benzene solvate (1·8 g) of (22) slowly crystallised from the solution.

4-Amino-2-[2-(3,3-di-n-propyltriazen-1-yl)phenyl]quinazoline (23).—Prepared from 1,3-bis-*o*-cyanophenyltriazene in boiling di-n-propylamine alone (61% yield) or with benzene as solvent (85% yield), this *triazenylphenylquinazoline* crystallised from benzene–light petroleum as cream needles, m.p. 129—130° (efferv.) (Found: C, 69·3; H, 7·0; N, 23·8. $C_{20}H_{24}N_6$ requires C, 69·0; H, 6·9; N, 24·1%); $\nu_{max.}$ (KBr) 3485 and 3300 (NH), 2960 and 2865 (aliphatic CH), and 1645 cm^{-1} (C=N).

2,2′-[Piperazine-1,4-diylbis(azo-o-phenylene]bis-4-aminoquinazoline (24).—A dark brown solid was deposited when 1,3-bis-*o*-cyanophenyltriazene (3 g) was boiled in benzene (30 ml) containing piperazine (0·6 g). The quinazoline (24) (3·0 g) was collected, but could not be purified. It melted indefinitely over 100° (with efferv.) and was soluble in ethanol and chloroform, but insoluble in non-polar solvents. No satisfactory microanalytical figures were obtained.

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