Triazines and Related Products. Part 27.[1] Thermolysis of 4-Anilino-1,2,3-benzotriazines

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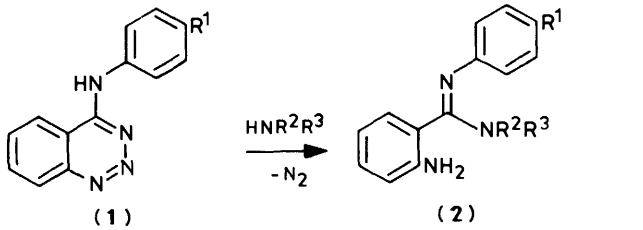
Thermolysis of 4-(4-cyanoanilino)-1,2,3-benzotriazine (**1a**) in morpholine affords 3-[2-amino-*N*-(4-cyanophenyl)benzimidoyl]-4-(4-cyanophenylimino)-3,4-dihydro-1,2,3-benzotriazine (**3a**) in addition to the major product 2-amino-N^2-(4-cyanophenyl)-N^1N^1-oxydiethylenebenzamidine (**2a**). The yield of (**3a**) increases if high boiling non-nucleophilic solvents are employed as the thermolysis medium. Decomposition of (**3a**) in hot acetic acid affords derivatives of 4-(4-cyanophenyl)-2-phenylquinazoline.

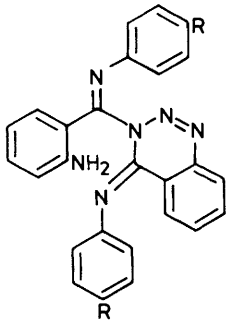
Interaction of a series of substituted 4-anilino-1,2,3-benzotriazines and boiling heteroalicyclic secondary amines (pyrrolidine, piperidine, and morpholine) affords high yields of 2-amino-N^2-aryl-N^1N^1-disubstituted benzamidines.[2] In one instance, the reaction of 4-(4-cyanoanilino)-1,2,3-benzotriazine (**1a**) in morpholine, the amidine (**2a**) was accompanied by a high melting yellow by-product (*ca.* 17%). This paper is concerned with the determination of the structure of this by-product and the mechanism of its formation.



(**1**)
a; R^1 = CN
b; R^1 = NO_2

(**2**)

	R^1	R^2	R^3
a;	CN	$-[CH_2]_2O[CH_2]_2-$	
b;	CN	$-[CH_2]_4-$	
c;	CN	$-[CH_2]_5-$	
d;	NO_2	$-[CH_2]_2O[CH_2]_2-$	



(**3**)
a; R = CN
b; R = NO_2

When 4-(4-cyanoanilino)-1,2,3-benzotriazine (**1a**) was boiled in pyrrolidine or piperidine no coloured by-products were isolated: the only products were the amidines (**2b**) and (**2c**) formed in 70 and 88% yield respectively. The amidine (**2a**) was not a precursor of the yellow material since this compound and its analogues (**2b** and **c**) were recovered unchanged after being boiled for prolonged periods in morpholine.

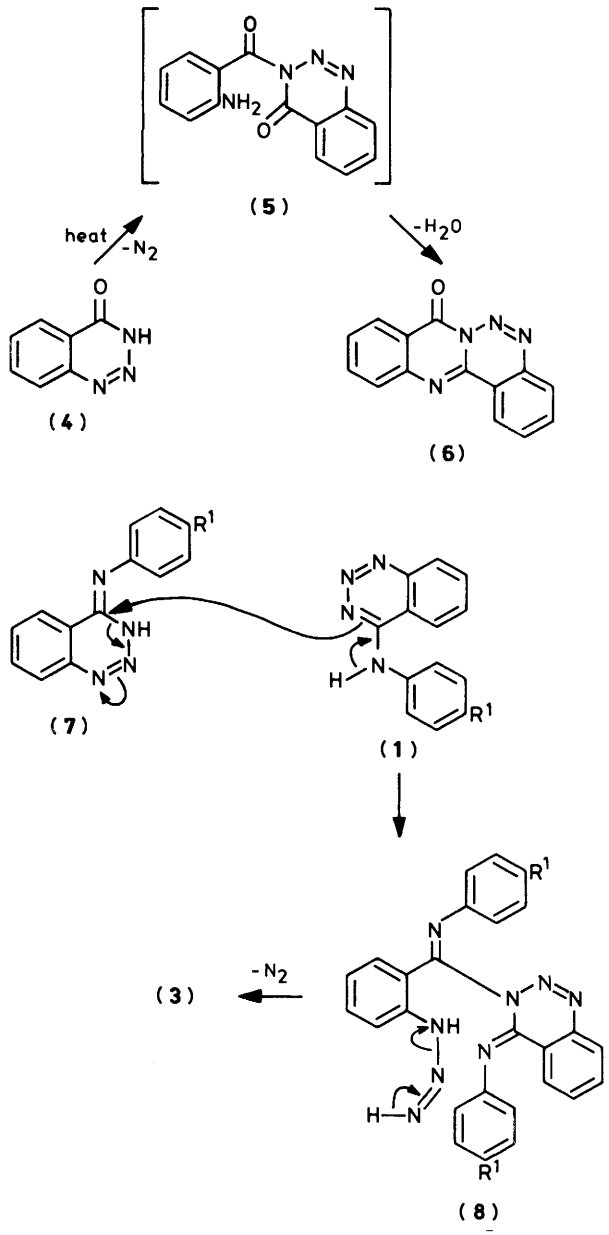
Elemental analysis of the yellow product indicated a molecular formula of $C_{28}H_{18}H_8$, corresponding to two molecules of starting material minus two nitrogen atoms; the electron-impact-promoted mass spectrum showed a highest mass ion at *m/z* 438 ($C_{28}H_{18}N_6$) corresponding to ($M^{+\cdot} - N_2$). The i.r. spectrum of the product showed N–H and C≡N absorptions and an intact NNN linkage was identified by the development of a red azo-dye when the yellow product was heated with 2-naphthol in 2M-hydrochloric acid. The yellow product melted at 246—248 °C with effervescence, again indicative of the presence of an NNN linkage. Taking all the evidence into account structure (**3a**) is proposed for the yellow product obtained from (**1a**) in morpholine, and (**3b**) for the corresponding nitro-analogue formed in low yield (4%) together with the amidine (**2d**) (90%) when 4-(4-nitroanilino)-1,2,3-benzotriazine (**1b**) was boiled in morpholine.

1,2,3-Benzotriazines of structure (**3**) are unique and their nearest relatives are the 3-alkyl- and 3-aryl-4-arylimino-1,2,3-benzotriazines formed upon diazotisation of 2-amino-N^1N^2-disubstituted benzamidines.[3]

It seemed plausible that the higher boiling point of morpholine compared with that of pyrrolidine and piperidine was instrumental in diverting the reaction course away from benzamidine formation. This view was sustained when higher yields of the yellow by-product (**3a**) were formed when (**1a**) was heated in higher boiling solvents (Table 1). These experiments served to confirm that the morpholine did not participate in covalent events leading to by-product formation.

The mechanism of these 1,2,3-benzotriazine decompositions is probably analogous to that proposed to account for the thermal conversion of 1,2,3-benzotriazin-4(3*H*)-one (**4**) to the tetracyclic triazine (**6**) *via* the anthraniloylbenzotriazinone (**5**).[4,5] Thus attack by a molecule of the anilinobenzotriazine (**1**) at C-4 of the arylimino tautomer (**7**) of another molecule leads to ring-opening and the formation of an unstable 3-aryltriazene (**8**) which loses nitrogen to yield the observed product (**3**) (Scheme 1).

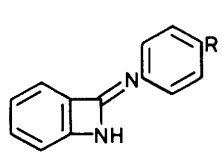
It is rather surprising that products of type (**3**) are formed in the reactions of 4-anilinobenzotriazines (**1a** and **b**) in morpholine since this nucleophilic reactant is present in large excess. Only those substrates bearing $-M$ substituents in the anilino moeity yield unusual products:[2] this structural feature evidently increases the electron deficiency at C-4, allowing the weakly nucleophilic anilinobenzotriazine to compete effectively



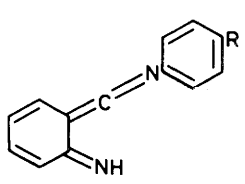
Scheme 1.

with the morpholine. In the absence of a nucleophilic solvent (*e.g.* in diethyleneglycol dimethyl ether) the yield of thermolysis product (**3a**) from (**1a**) is markedly increased (Table 1).

Because degradation of the anilinobenzotriazines (**1a** and **b**) takes place substantially below their melting (decomposition) points (229 and 237 °C respectively)[6] it is unlikely that the initial event is heterolysis of the NNN linkage leading to a benzazetineimine (**9**) or its valence tautomer (**10**), although this



(**9**)



(**10**) **a**; R = CN
b; R = NO_2

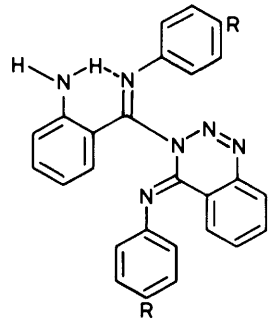
Table 1. Products formed from 4-(4-cyanoanilino)-1,2,3-benzotriazine (**1a**) in boiling solvents.

Solvent	B.p. (°C)	Reaction time (h)	Product	Yield (%)
Pyrrolidine	86—87	8	(**2b**)[a]	70
Piperidine	104—107	7	(**2c**)[b]	88
Morpholine	124—128	7	(**2a**)[c]	80
			(**3a**)[c]	17
N-Methylpiperazine	137—140	8	(**3a**)[d]	30
2,6-Dimethylmorpholine	147	8	(**3a**)[d]	50
Diethylene glycol dimethyl ether	159—162	2	(**3a**)	70
Collidine	170—175	1.5	(**3a**)	70
Aniline	184	0.5	(**3a**)	60

[a] This product, 2-*amino*-N^2-(4-*cyanophenyl*)-N^1N^1-*tetramethylenebenzamidine* had m.p. 95—97 °C (Found: C, 72.8; H, 6.1; N, 18.6%; M^+, 290. $C_{18}H_{18}N_4 \cdot 0.25H_2O$ requires C, 73.1; H, 6.5; N, 19.9%; *M*, 290); $\nu_{max.}$(KBr) 2 213 cm^{-1} (CN). [b] This product, 2-amino-N^2-(4-cyanophenyl)-N^1N^1-pentamethylenebenzamidine, was identical (m.p. and i.r.) with an authentic sample.[6] [c] See Experimental section. [d] Products also included the corresponding 2-amino-N^2-(4-cyanophenyl)-N^1N^1-(substituted)benzamidine but this was not characterized.

possibility cannot be excluded: these labile species would, of course, react with amines to form amidines (**2**) and with undecomposed substrate to afford by-products (**3**).

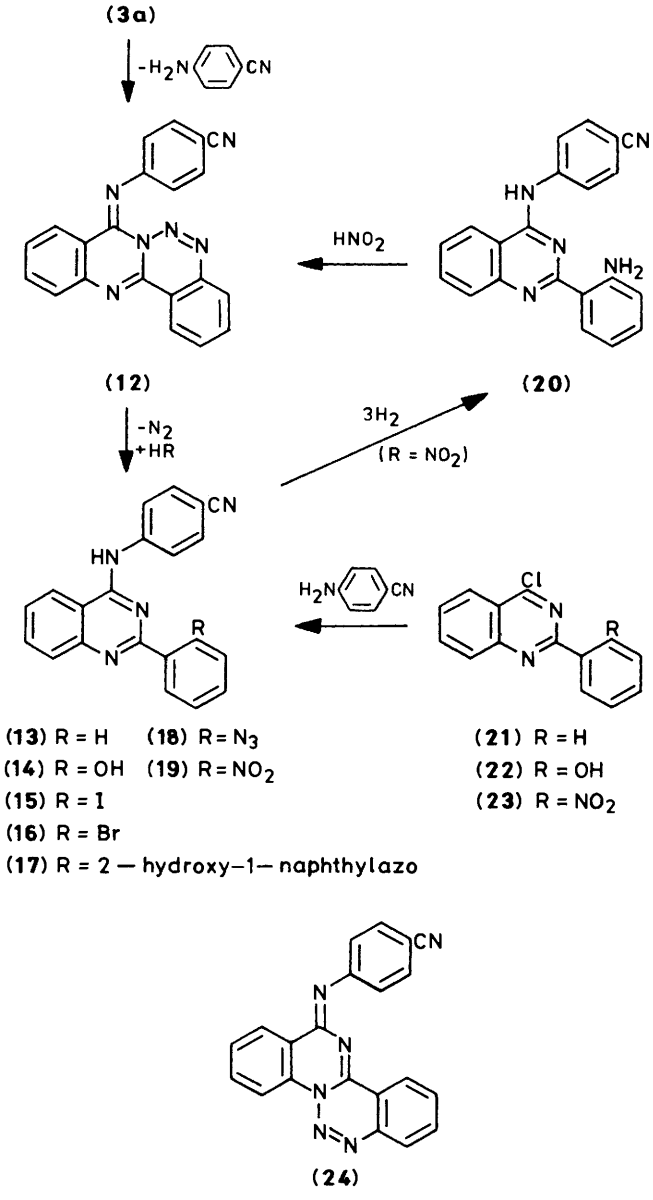
It is also surprising that compounds (**3a** and **b**) do not undergo further cyclisation to tetracycles with the liberation of 4-cyano- and 4-nitro-aniline respectively under the thermolytic conditions. Possibly the 1,2,3-benzotriazines (**3a** and **b**) exist as H-bonded rotamers (**11a** and **b**) because of the steric crowding imposed by the two arylimino groups and this restrains the free amino group from orthogonal attack at C-4 of the triazine ring. Even more surprisingly, compound (**3a**) was recovered unchanged after being boiled in 2M-sodium hydroxide for 6 h.



(**11**) **a**; R = CN
b; R = NO_2

Cyclisation of the benzotriazine (**3a**) was achieved eventually under acidic conditions. In boiling acetic acid (6 h), or more prolonged boiling in an acetic acid–ethanol mixture, (**3a**) afforded 4-(4-cyanoanilino)-2-phenylquinazoline (**13**). In boiling 2M-hydrochloric acid or 2M-sulphuric acid the product was the 2-(2-hydroxyphenyl)quinazoline (**14**): 4-cyanoaniline was detected (t.l.c.) as a by-product in the reaction mixtures from the mineral acid decompositions. Likewise, decomposition of (**3a**) in boiling acetic acid containing either sodium iodide or hydriodic acid gave the 2-(2-iodophenyl)quinazoline (**15**) in high yield; decomposition in acetic–hydrobromic acid likewise afforded the bromophenylquinazoline (**16**); and incorporation of 2-naphthol in the hot acetic acid medium led to the formation

of the naphthylazo-dye (**17**). Degradation of (**3a**) in acetic acid containing sodium azide gave a sample of crude 2-(2-azidophenyl)quinazoline (**18**) which decomposed on subsequent crystallization. Samples of the quinazolines (**13**) and (**14**) were synthesized independently by treating the 4-chloroquinazolines (**21**) and (**22**), respectively, with 4-cyanoaniline in acetone, and were proved to be identical with the products prepared by degradation of (**3a**).



Scheme 2.

Although the exact timing of cyclisation and diazo-displacement in these reactions of compound (**3a**) is not certain we propose that the tetracyclic triazine (**12**) participates as an intermediate (Scheme 2). An authentic sample of (**12**) was prepared starting from 4-chloro-2-(2-nitrophenyl)quinazoline (**23**) which was firstly treated with 4-cyanoaniline to afford the 4-cyanoanilinoquinazoline (**19**). Catalytic hydrogenation of (**19**) over a palladium–charcoal catalyst yielded the corresponding amine (**20**) which, when diazotized in sulphuric acid, liberated the tetracyclic triazine (**12**) upon basification. Although an alternative cyclisation at N-1 of the quinazoline ring leading to an isomeric tetracyclic triazine (**24**) cannot be excluded, previous experiences in related polycyclic quinazoline chemistry have shown that N-3, exclusively, of the quinazoline is the site for ring-closure.[7,8]

Finally, support for the proposed intermediacy of the tetracyclic triazine (**12**) in the degradations of compound (**3a**) was forthcoming when a pure sample of (**12**) was subjected to decompositions in ethanol, acetic acid, mineral acids, or acetic acid containing iodide, bromide, or azide ions, and 2-naphthol. The products were identical with the 4-(4-cyanoanilino)-2-[2-(substituted)phenyl]quinazolines previously isolated when compound (**3a**) was decomposed under identical conditions, and their electronic absorption spectra (Table 2) displayed the expected familial relationships.

Table 2. Electronic absorption spectra of substituted 4-(4-cyanoanilino)-2-phenylquinazolines[a]

Compound	$\lambda_{max.}$(nm) (in 95% ethanol)
(**13**)	256, 279, 326, 340, 352
(**14**)	258, 278,* 325,* 339, 354
(**15**)	260, 288, 330, 340, 355*
(**16**)	244, 260,* 280,* 325,* 341, 355*
(**18**)	235, 256,* 287, 325,* 338, 353*
(**19**)	230, 250,* 275,* 325,* 337, 350*
(**20**)	235, 257,* 288, 329, 340,* 353*

[a] Recorded on a Unicam SP 8000 spectrophotometer. * Denotes inflexion.

Experimental

Light petroleum refers to that fraction boiling in the range 60—80 °C.

3-[2-*Amino*-N-(4-*cyanophenyl*)*benzimidoyl*]-4-(4-*cyanophenylimino*)-3,4-*dihydro*-1,2,3-*benzotriazine* (**3a**).—A solution of 4-(4-cyanoanilino)-1,2,3-benzotriazine (**1a**) (4.8 g)[6] in morpholine (50 ml) was boiled for 7 h and then kept at 4 °C for 10 d. The precipitated yellow *benzotriazine* (**3a**) (1.2 g) was collected and washed with acetone and hot toluene. The purified product had m.p. 246—248 °C (efferv.) [Found: C, 71.85; H, 3.7; N, 23.8%; *m/z* 438.1592 ($M^+ - N_2$). $C_{28}H_{18}N_8$ requires C, 71.1; H, 3.9; N, 24.0%; *m/z* 438.159 6 ($M - N_2$)]; $\nu_{max.}$(KBr) 3 370 (NH) and 2 228 cm^{-1} (C≡N). The morpholine-soluble material was recovered by vacuum evaporation of the solvent and crystallized from benzene–light petroleum to yield 2-amino-N^2-(4-cyanophenyl)-N^1N^1-oxydiethylenebenzamidine (**2a**) (3.6 g) which was identical (m.p. and i.r.) with an authentic sample.[2] The *NN*-oxydiethylenebenzamidine (**2a**) was recovered unchanged after being boiled in morpholine for 3 h.

The benzotriazine (**3a**) was also prepared by boiling 4-(4-cyananilino)-1,2,3-benzotriazine (**1a**) in a range of organic solvents (Table 1).

3-[2-*Amino*-N-(4-*nitrophenyl*)*benzimidoyl*]-4-(4-*nitrophenylimino*)-3,4-*dihydro*-1,2,3-*benzotriazine* (**3b**).—A solution of 4-(4-nitroanilino)-1,2,3-benzotriazine (**1b**) (4.5 g)[6] in morpholine (20 ml) was boiled; the benzotriazine slowly dissolved to give a red solution. After 10 h the solution was shaken with toluene (50 ml) and water (50 ml). A brown insoluble material (0.1 g) was collected, washed with acetone and water, and crystallized from dimethylformamide to furnish the *dihydrobenzotriazine dimethylformamide solvate* as ochre rosettes, m.p. 275 °C (efferv.) [Found: C, 60.2; H, 4.4; N, 22.0%; *m/z* 478.1389 ($M^+ - N_2$). $C_{26}H_{18}N_8O_4 \cdot C_3H_7NO$ requires C, 60.1; H, 4.3; N, 21.8%;

m/z 478.1371 ($M - N_2$)]; $\nu_{max.}$(KBr) 3 320 (NH) and 1 665 cm^{-1} (C=O).

The toluene–water mixture was separated and the aqueous layer was re-extracted with toluene (2 × 50 ml). The combined toluene fractions were dried (anhydrous sodium sulphate) and evaporated to yield a crystalline residue (4.6 g) which recrystallized from toluene–light petroleum to afford 2-*amino*-N^2-(4-*nitrophenyl*)-N^1N^1-*oxydiethylenebenzamidine* (**2d**) as yellow leaflets, m.p. 170—171 °C (Found: C, 62.5; H, 5.7; N, 17.0. $C_{17}H_{18}N_4O_3$ requires C, 62.6; H, 5.5; N, 17.2%).

8-(4-*Cyanophenylimino*)-8H-*quinazolino*[3,2,c][1,2,3]*benzotriazine* (**12**).—A mixture of 4-chloro-2-(2-nitrophenyl)-quinazoline (**23**) (2.85 g),[8] 4-cyanoaniline, and 10M-hydrochloric acid (0.2 ml) was boiled in acetone (2 h). The product 4-(4-*cayanoanilino*)-2-(2-*nitrophenyl*)*quinazoline* (**19**) (3.2 g), formed white crystals from ethanol–acetic acid, m.p. 234—235 °C (Found: C, 68.6; H, 3.5; N, 19.1%; M^+, 367. $C_{21}H_{13}N_5O_2$ requires C, 68.7; H, 3.5; N, 19.1%; *M*, 367); $\nu_{max.}$(KBr) 2 240 cm^{-1} (CN). The *dihydrochloride salt*, formed from the base in 10M-hydrochloric acid, had m.p. 262—265 °C (Found: C, 55.3; H, 3.45; N, 15.3. $C_{21}H_{13}N_5O_2 \cdot 2HCl \cdot H_2O$ requires C, 55.1; H, 3.7; N, 15.3%).

Catalytic hydrogenation of a solution of the nitrophenylquinazoline base (**19**) (0.4 g) in acetic acid (120 ml) over a 10% palladium–charcoal catalyst (0.15 g) at 2 atm. afforded 2-(2-*aminophenyl*)-4-(4-*cyanoanilino*)*quinazoline* (**20**), which crystallized from aqueous acetic acid as a *hydrate*, m.p. 220—225 °C (decomp.) (Found: C, 71.0; H, 4.35; N, 19.9%; M^+, 337. $C_{21}H_{15}N_5 \cdot H_2O$ requires C, 71.0; H, 4.7; N, 19.75%; *M*, 337); $\nu_{max.}$(KBr) 2 230 cm^{-1} (CN).

A solution of the aminophenylquinazoline (**20**) (0.17 g) in 10M-sulphuric acid (5 ml) was diazotized with a solution of sodium nitrite (0.07 g) in water (3 ml) at 0 °C. The mixture was stirred for 2 h at 0 °C and then basified with concentrated aqueous ammonia. After 1 h the *quinazolinobenzotriazine* (**12**) (0.16 g) was collected and crystallized from ethanol with m.p. 205—210 °C (efferv.) (Found: C, 69.8; H, 3.5; N, 22.7%; M^+, 348. $C_{21}H_{12}N_6 \cdot 0.75H_2O$ requires C, 69.8; H, 3.7; N, 23.2%; *M*, 348); $\lambda_{max.}$(EtOH) 240 (infl.), 250, 278 (infl.), 340 (infl.), and 352 nm; $\nu_{max.}$(KBr) 2 220 cm^{-1} (CN).

4-(4-*Cyanoanilino*)-2-*phenylquinazoline* (**13**).—(i) 4-Chloro-2-phenylquinazoline (**21**) (1.2 g) and 4-cyanoaniline (1.18 g) were refluxed in acetone (150 ml) containing 10M-hydrochloric acid (0.2 ml) for 1 h. The precipitated buff solid was collected, washed in turn with dilute aqueous ammonia and water, and the product was crystallized from aqueous acetic acid to afford the *phenylquinazoline* (**13**) (90%), m.p. 206—207 °C (Found: C, 76.4; H, 4.65; N, 16.5%; M^+, 322.121 84. $C_{21}H_{14}N_4 \cdot 0.5H_2O$ requires C, 76.1; H, 4.5; N, 16.9%; *M* 322.121 199); $\nu_{max.}$(KBr) 2 225 cm^{-1} (CN). The *dihydrochloride salt*, formed from the base in 10M-hydrochloric acid, had m.p. 270—272 °C (Found: C, 64.0; H, 4.1; N, 14.3. $C_{21}H_{14}N_4 \cdot 2HCl$ requires C, 63.95; H, 4.06; N, 14.2%).

(ii) The same (i.r. and u.v.) phenylquinazoline (90 and 88% yield respectively) was formed when compound (**3a**) (0.3 g) was boiled in acetic acid (6.0 ml) for 6 h or in a mixture of acetic acid–ethanol(4:1) for 48 h.

(iii) When the quinazolinobenzotriazine (**12**) (0.3 g) was boiled in ethanol (6.0 ml) for 24 h the product (**13**) (90%) was identical (i.r. and u.v.) with the aforementioned samples.

4-(4-*Cyanoanilino*)-2-(2-*hydroxyphenyl*)*quinazoline* (**14**).—(i) 4-Chloro-2-(2-hydroxyphenyl)quinazoline (**22**) (1.2 g) and 4-cyanoaniline (1.18 g) were refluxed in acetone (150 ml) containing 10M-hydrochloric acid (0.2 ml) for 1 h. The cooled solution deposited the *hydroxyphenylquinazoline* which was collected and washed with dilute aqueous ammonia. The crude product crystallized from aqueous acetic acid as a *hydrate* (1.6 g), m.p. 212—215 °C (Found: C, 70.65; H, 3.4; N, 15.9%; M^+, 338. $C_{21}H_{14}N_4O \cdot H_2O$ requires C, 70.8; H, 4.5; N, 15.7%; *M*, 338); $\nu_{max.}$(KBr) 2 230 cm^{-1} (CN).

(ii) The same hydroxyphenylquinazoline (0.25 and 0.2 g respectively) was formed when the benzotriazine (**3a**) (0.5 g) was boiled in 2M-hydrochloric acid (10 ml) for 1 h, or in 2M-sulphuric acid (10 ml) for 1 h. T.l.c. examination of the reaction mixture [silica gel; toluene–acetone (3:1) as developing solvent] revealed the presence of 4-cyanoaniline which co-chromatographed with an authentic sample.

(iii) A sample of the hydroxyphenylquinazoline (0.28 g), identical (i.r. and u.v.) with the aforementioned samples, was obtained when the quinazolinobenzotriazine (**12**) (0.5 g) was boiled in 4M-sulphuric acid (10 ml) for 1 h.

4-(4-*Cyanoanilino*)-2-(2-*iodophenyl*)*quinazoline* (**15**).—(i) The benzotriazine (**3a**) (0.26 g) was heated under reflux in acetic acid (10 ml) containing sodium iodide (0.7 g) for 2.5 h. The cooled mixture deposited a violet solid which decolourized when it was rinsed with acetone. The *iodophenylquinazoline* (**15**) (0.18 g) formed golden crystals (from ethanol) of the *hydrate*, m.p. 230—232 °C (Found: C, 53.6; H, 3.3%; M^+, 447. $C_{21}H_{13}IN_4 \cdot H_2O$ requires C, 54.0; H, 3.2%; *M*, 447); $\nu_{max.}$(KBr) 2 220 cm^{-1} (CN).

The same iodophenylquinazoline (52%) was formed when the benzotriazine (**3a**) was heated in acetic acid (10 ml) containing hydriodic acid (57% aqueous solution; 1 ml) for 20 min.

(ii) When the quinazolinobenzotriazine (**12**) was heated with hydriodic acid in acetic acid the same (u.v. and i.r.) iodophenylquinazoline (65%) was isolated.

2-(2-*Bromophenyl*)-4-(4-*cyanoanilino*)*quinazoline* (**16**).—(i) The benzotriazine (**3a**) (0.4 g) was refluxed in a mixture of acetic acid (5 ml) and 45% hydrobromic acid in acetic acid (1 ml) for 1 h. The crude *bromophenylquinazoline dihydrobromide* was purified by acetone reprecipitation from an aqueous solution and afforded a pure product (0.32 g) with m.p. 260 °C (decomp.) (Found: C, 44.7; H, 2.6%; M^+, 399/401. $C_{21}H_{13}BrN_4 \cdot 2HBr$ requires C, 44.7; H, 2.6%; *M*, 399/401 as the molecular ion of the base); $\nu_{max.}$(KBr) 2 220 cm^{-1} (CN).

The *free base sesquihydrate*, m.p. 166—168 °C (from ethanol), was formed from the dihydrobromide salt and dilute aqueous ammonia (Found: C, 59.3; H, 3.7; N, 13.7%; M^+, 399/401. $C_{21}H_{13}BrN_4 \cdot 1.5H_2O$ requires C, 58.9; H, 3.7; N, 13.1%; *M*, 399/401); $\nu_{max.}$(KBr) 2 210 cm^{-1} (CN).

(ii) The same (i.r. and u.v.) bromophenylquinazoline free base (**16**) (85%) was isolated when the quinazolinobenzotriazine (**12**) was heated in hydriodic–acetic acid under the conditions described above and the crude dihydrobromide salt was triturated with aqueous ammonia.

4-(4-*Cyanoanilino*)-2-[2-(2-*hydroxy*-1-*napthylazo*)*phenyl*]-*quinazoline* (**17**).—(i) The benzotriazine (**3a**) (0.35 g) and 2-naphthol (0.15 g) were boiled in acetic acid (10 ml) for 2 h. The orange *azophenylquinazoline* (**17**) (0.3 g) was crystallized from ethanol and had m.p. 320 °C (decomp.) (Found: C, 73.3; H, 3.9; N, 17.0. $C_{31}H_{20}N_6O \cdot H_2O$ requires C, 73.0; H, 4.3; N, 16.5%); $\nu_{max.}$(KBr) 2 240 cm^{-1} (CN).

(ii) The same (i.r. and u.v.) azo-dye (68%) was formed when the quinazolinobenzotriazine (**12**) was heated with 2-naphthol in acetic acid as above.

2-(2-*Azidophenyl*)-4-(4-*cyanoanilino*)*quinazoline* (**18**).—(i) A mixture of the benzotriazine (**3a**) (0.26 g) and sodium azide (0.065 g) was boiled in acetic acid for 3 h. The orange product (0.15 g) was washed with water and dried. The crude azidophenylquinazoline (**18**) had m.p. 210—212 °C (efferv.)

(Found: M^+, 363. $C_{21}H_{13}N_7$ requires M, 363); $\nu_{max.}$(KBr) 2 250 (CN), and 2 140 and 2 160 cm^{-1} (N_3).

Repeated crystallization of the azide from aqueous acetic acid afforded a pure sample of 2-(2-aminophenyl)-4-(4-cyanoanilino)quinazoline hydrate (**20**)·H_2O, m.p. 220—225 °C (decomp.), identical (i.r. and u.v.) with the sample described above.

(ii) When the quinazolinobenzotriazine (**12**) was heated with sodium azide in acetic acid under identical conditions the same crude azide (**18**) was isolated. This was transformed into the corresponding amine (**20**) on recrystallization from aqueous acetic acid.

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Received 3*rd October* 1983; *Paper* 3/1737