Triazines and Related Products. Part X.[1] A Re-examination of the Reaction between Benzil and Diaminoguanidine Nitrate

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Benzil reacts with diaminoguanidine nitrate to yield the nitrate salt of benzil mono[(aminoamidino)hydrazone] (2). The hydrazone (2) is unstable, and cyclises on melting or in solvents to 5,6-diphenyl-3-hydrazino-1,2,4-triazine (3). Diazotisation of the hydrazone (2) and of hydrazine (3) affords the same product, 6,7-diphenyltetrazolo-[1,5-*b*]-*as*-triazine (9) which decomposes in boiling secondary amines to yield substituted 3-amino-5,6-diphenyl-1,2,4-triazines and hydrazoic acid. Both the hydrazone (2) and the hydrazine (3) react with triethyl orthoformate or formic acid to give 6,7-diphenyltriazolo[4,3-*b*]-*as*-triazine (16), which was also prepared, unambiguously, from benzil and 3,4-diamino-1,2,4-triazole. Although conditions favourable for Dimroth rearrangement were employed, no such transformations were encountered in the reactions of the bicyclic systems (9) and (16).

3-AMINO-5,6-DIPHENYL-1,2,4-TRIAZINE (1a) has been prepared from benzil and aminoguanidine,[2] and the reaction between α-dicarbonyl compounds and aminoguanidine has wide applicability in the synthesis of monocyclic 1,2,4-triazines, and triazines fused to carbo- or hetero-cyclic systems.[3,4] The reaction between α-dicarbonyl compounds and diaminoguanidine, in contrast, has been little studied, although with benzil for example the mono[(aminoamidino)hydrazone] (2) which is presumably formed initially could cyclise with the involvement of amidino or hydrazino nitrogen atoms to afford either the isomeric 1,2,4-triazines (3) and (4) or the tetrazepine (5). Clearly, the basicity of the attacking nucleophile and the pH of the medium should influence the direction of cyclisation.

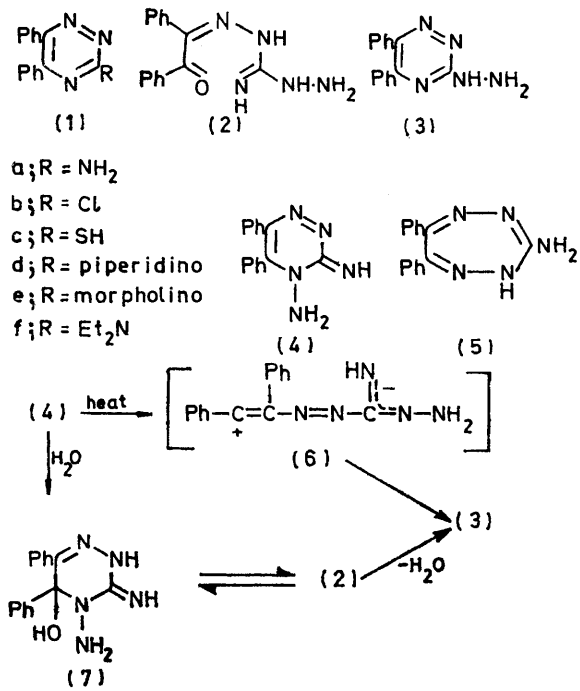
In a preliminary examination of this reaction Lieber and Strojny[5] obtained a product (85%) from benzil and diaminoguanidine nitrate which they formulated as the nitrate salt of benzil mono[(aminoamidino)-hydrazone] (2) on the basis of a nitrogen analysis. This salt reacted with benzaldehyde to give a low yield of the benzylidene derivative of the hydrazine (3), and, on being neutralised with sodium acetate in methanol afforded a yellow compound, m.p. 173—175°, which was assigned the empirical formula $C_{15}H_{15-16}N_4$ on analytical evidence. As the authors were 'unable to account for the loss of an atom of nitrogen or for the high hydrogen content' a re-examination of this reaction appeared desirable.

In the present work the product originally formulated as the nitrate of the hydrazone (2) was readily obtained, albeit in a lower yield than previously.[5] Careful basification of the nitrate yielded an off-white base which melted at 96—98°, resolidified, and finally re-melted at 171—173°. The high-melting solid was identical with the product formed from 3-chloro-5,6-diphenyl-1,2,4-triazine (1b) and hydrazine,[6] and is accordingly identified as the hydrazinotriazine (3). Attempts to crystallise the low-melting solid for analysis from methyl or ethyl alcohols, benzene, or chloroform led exclusively to the isolation of the hydrazine (3); basification of 'benzil mono(aminoguanyl)hydrazone nitrate' according to the procedure of Lieber and Strojny[5] also resulted in the formation of the hydrazine (3) and *not* the compound $C_{15}H_{15-16}N_4$. The base of m.p. 96—98° formed a stable toluene-*p*-sulphonate, which, like the nitrate,[5] gave analytical figures expected for a salt of hydrazone (2). An absorption at 1650 cm^{-1} in the i.r. spectrum of the base appeared to confirm the presence of a carbonyl group (*cf.* $\nu_{C=O}$ at 1660 for benzil and at 1645 cm^{-1} for benzil monohydrazone). However, this interpretation is open to doubt, as many of the 3-substituted 1,2,4-triazines examined in the present work exhibited C=N absorptions in this region. Indeed, the foregoing analytical and chemical results can be accommodated satisfactorily if the compound of m.p. 96—98° were the hydrate (covalent or solvated) of 4-amino-3,4-dihydro-3-imino-5,6-diphenyl-1,2,4-triazine (4)—1,2,4-triazines are known to have a propensity to form water adducts.[7] The *N*-amine (4) is structurally related to many *N*-alkyl heterocycles in which the alkyl group rearranges from an endo- to an exo-cyclic position *via* an acyclic intermediate (Dimroth rearrangement).[8] Analogous transformation of the *N*-amine (4) could proceed thermally *via* the zwitterion (6) or, alternatively, *via* the covalent hydrate (7), which is tautomeric with the hydrazone (2); in either case the rearrangement product would be the observed hydrazine (3) as shown in Scheme 1.

The mass spectra of 3-substituted 5,6-diphenyl-1,2,4-triazines (Table) exhibit abundant molecular ions, and the dominant fragmentation leads to the formation of the highly delocalised diphenylacetylene radical ion at *m/e* 178, which is the base peak in all cases.[9] Benzil and its acyclic derivatives in contrast show molecular ions of low intensity, and major peaks attributable to the phenylacylium ion (*m/e* 105) and the phenyl cation (*m/e* 77). In the mass spectrum of the compound of

[1] Part IX, S. M. Mackenzie and M. F. G. Stevens, *J.C.S. Perkin I*, 1972, 295.
[2] J. A. Elvidge, G. T. Newbold, I. R. Senciall, and T. G. Symes, *J. Chem. Soc.*, 1964, 4157.
[3] J. G. Erickson, *J. Amer. Chem. Soc.*, 1952, **74**, 4706.
[4] F. Kurzer and L. E. A. Godfrey, *Angew. Chem. Internat. Edn.*, 1963, **2**, 459.
[5] E. Lieber and E. J. Strojny, *J. Org. Chem.*, 1952, **17**, 518.
[6] P. V. Laakso, R. Robinson, and H. P. Vandrewala, *Tetrahedron*, 1957, **1**, 103.
[7] W. W. Paudler and T-K. Chen, *J. Heterocyclic Chem.*, 1970, **7**, 767.
[8] D. J. Brown, 'Mechanisms of Molecular Migrations,' ed. S. Thyagarajan, vol. 1, Wiley, New York, 1968, p. 209.
[9] M. H. Palmer, P. N. Preston, and M. F. G. Stevens, *Org. Mass Spectrometry*, 1971, **5**, 1085.

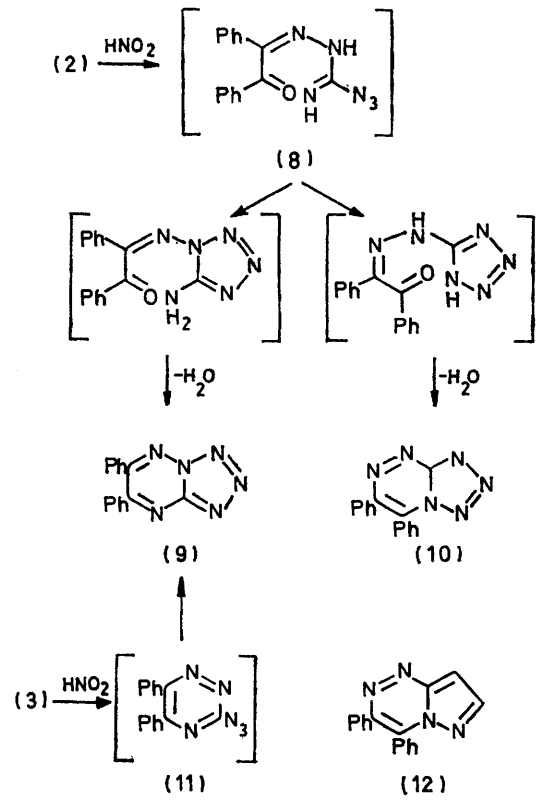
m.p. 96—98°, no molecular ion corresponding to benzil mono[(aminoamidino)hydrazone] (2) was observed, and



SCHEME 1

the spectrum was nearly identical with that of the hydrazine (3), with a base peak at *m/e* 178 typical of a cyclic system. The behaviour of the compound of m.p. 96—98° towards nitrous acid (Scheme 2) however, unequivocally establishes that it is the hydrazone (2) as proposed by Lieber and Strojny;[5] ion-impact-promoted decomposition of (2) must therefore be preceded by thermal cyclisation to the hydrazine (3). The lower intensity of the ion at *m/e* 178, and the higher abundance of ions at *m/e* 105 and 77 in the spectrum of benzil monothiosemicarbazone, presumably reflect the greater resistance of this compound (m.p. 185°)[10] to thermal cyclisation to the 3-mercaptotriazine (1c).

Diazotisation of the compound of m.p. 96—98° in either 2N-hydrochloric acid or 20% hypophosphorous acid did not afford 3-amino-5,6-diphenyl-1,2,4-triazine (1a), which would be expected if the compound were the solvated hydrate of the *N*-amine (4) or the covalent hydrate (7).[11] Instead, the crude product exhibited i.r. absorptions (KBr) at 2140 (N_3) and 1670 cm^{-1} (C=O), and bands characteristic of a tetrazolotriazine. The azide and carbonyl bands decreased in intensity when the solid was stored at room temperature, and more rapidly in boiling ethanol. These absorptions are attributed to the azidohydrazone (8), and, depending on the direction of cyclisation of the azide group, two tetrazolotriazines (9) and (10) are possible. Only one product was detected (t.l.c.) and this was assigned the tetrazolo[1,5-*b*]-*as*-triazine structure (9) because its electronic absorption spectrum (see Figure) differed



SCHEME 2

Relative intensities (% of base peak) of significant ions recorded on an A.E.I.–G.E.C. MS 902 instrument operating at 70 eV, with a source temperature in the range 100—150° (unless otherwise stated)

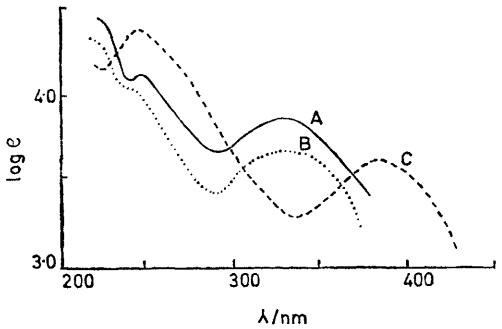
Compound	Molecular ion	PhC≡C·Ph$_2^{+\cdot}$ *m/e* 178	PhC≡O$^+$ *m/e* 105	Ph$^+$ *m/e* 77
(1a)	20 (*m/e* 248)	100		5
(1b) [a]	16 (*m/e* 269) 50 (*m/e* 267)	100		11
(1c) [a]	37 (*m/e* 265)	100		8
(1d)	9 (*m/e* 316)	100		4
(1e)	63 (*m/e* 318)	100		7
(1f)	37 (*m/e* 304)	100		2
(3) [a]	97 (*m/e* 263)	100		8
(12) [a]	100 (*m/e* 249)	87		14
(13)	25 (*m/e* 548)	100		1
Benzil [b]	<1 (*m/e* 210)		100	24
Benzil hydrazone [b,c]	2 (*m/e* 224)		15	80
Benzil monothiosemicarbazone [b]	Not observed [d]	10	33	80
Compound of m.p. 96—98°: benzil mono-(aminoamidino)-hydrazone [b]	Not observed [e]	100	3	7

[a] Ref. 9. [b] Ion source at 50°. [c] Base peak at *m/e* 119. [d] Highest mass ion at *m/e* 249 (2%), base peak at *m/e* 162, and further major ion at *m/e* 119 (75%). [e] Highest mass ion at *m/e* 263 (90%).

[10] M. Gianturco and A. Romeo, *Gazzetta*, 1953, **82**, 429 (*Chem. Abs.*, 1954, **48**, 2074e).

[11] A. Dornow, H. Pietsch, and P. Mark, *Chem. Ber.*, 1964, **97**, 2647.

significantly from that of the pyrazolo[5,1-*c*]-*as*-triazine (12). The long-wavelength absorption of pyrazolotriazines related to (12) has been attributed to an electronic transition of the –N=N– chromophore in the



Electronic absorption spectra (ethanol) of 6,7-diphenyltetrazolo-[1,5-*b*]-*as*-triazine (A), 6,7-diphenyltriazolo[4,3-*b*]-*as*-triazine (B), and 3,4-diphenylpyrazolo[5,1-*c*]-*as*-triazine (C)

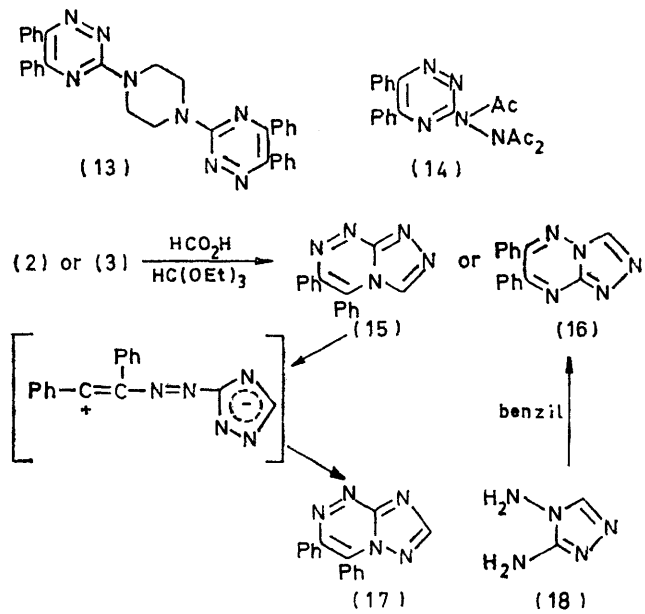
triazine ring [12]—its absence in the spectrum of the tetrazolotriazine formed from the hydrazone (2) therefore excludes the tetrazolo[5,1-*c*]-*as*-triazine structure (10).

The same tetrazole (9) was obtained by refluxing the chlorotriazine (1b) with sodium azide in aqueous acetone or, alternatively, by diazotising the hydrazine (3).[13] In the latter case, the i.r. spectrum of the crude solid product showed a weak band at 2136 cm^{-1} indicative of azide (11); this absorption disappeared when the solid was crystallised from ethanol. The preference for azide (11) to cyclise at N-2 of the triazine ring is paralleled by the behaviour of the aminotriazine (1a) towards oxidation; only the *N*(2)-oxide is produced, not the *N*(4)-oxide.[14]

In the search for evidence for the existence of a tetrazole (9) ⇌ azidotriazine (11) ⇌ tetrazole (10) equilibrium, the tetrazole (9) was boiled in acetic acid or pyridine: only the starting tetrazole was detected (t.l.c.). However, in boiling piperidine, morpholine, or diethylamine the tetrazole evolved hydrazoic acid with the formation of the substituted 3-aminotriazines (1d—f); with piperazine at 130° the product was the 1,4-disubstituted piperazine (13). Although displacement of azide ion from the intact tetrazole is a possibility, it seems more likely that ring opening to the azidotriazine (11) occurs: nucleophilic displacement of the azido-group by the secondary amines can be readily envisaged. Such a ready displacement of an azide group by nucleophiles recalls similar reactivity in 4-azidoquinoline *N*-oxide [15] and 9-azidoacridine quaternary salts.[16]

Because the hydrazone (2) cyclises to the hydrazine (3) in solvents, many of the reactions of these compounds lead to identical products. For example, both compounds react with benzaldehyde to afford the benzylidene derivative of the hydrazine (3); they afford the same triacetyl derivative (14) in acetic anhydride; they cyclise with formic acid or triethyl orthoformate to yield the same triazolotriazine. As in the case of the tetrazoles, cyclisation could involve either N-4 or N-2 of the triazine ring: the product would be the triazolo-[3,4-*c*]-*as*-triazine (15) or the [4,3-*b*]isomer (16), respectively. There are sufficient examples in the literature of bicyclic 1,2,4-triazoles to enable one to predict confidently that triazolotriazine (15) would be susceptible to Dimroth rearrangement to give the isomer (17) under the influence of heat, acid, or base (Scheme 3).[17]

The triazolotriazine obtained directly from the hydrazine (3), or, indirectly, from the hydrazone (2) was recovered unchanged after being maintained at its m.p. (1 h), or from boiling acetic acid, pyridine, or piperidine—structure (15) for this compound is therefore



SCHEME 3

excluded. The spectroscopic properties of the triazolotriazine are consistent with structure (16) not (17). The electronic absorption spectrum (Figure) was similar to that of the tetrazolotriazine (9) but different from that of the pyrazolotriazine (12). Reimlinger and Peiren [18] have shown that the triazole protons in a

[12] M. W. Partridge and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1966, 1127.
[13] (*a*) T. Sasaki, K. Kanematsu, and M. Murata, *J. Org. Chem.*, 1971, **36**, 446; (*b*) N. Takahayashi, *Yakugaku Zasshi*, 1955, **75**, 1242.
[14] W. W. Paudler and T-K. Chen, *J. Org. Chem.*, 1971, **36**, 787.
[15] S. Kamiya, *Chem. and Pharm. Bull.* (*Japan*), 1962, **10**, 669.
[16] A. C. Mair and M. F. G. Stevens, *J.C.S. Perkin I*, 1972, 161.
[17] R. G. W. Spickett and S. H. B. Wright, *J. Chem. Soc.* (*C*), 1967, 498; P. Guerret, R. Jacquier, and G. Maury, *J. Heterocyclic Chem.*, 1971, **8**, 643; G. W. Miller and F. L. Rose, *J. Chem. Soc.*, 1963, 5642; 1965, 3357; S. E. Mallett and F. L. Rose, *J. Chem. Soc.* (*C*), 1966, 2038; J. A. Bee and F. L. Rose, *ibid.*, p. 2031; K. T. Potts and E. G. Brugel, *J. Org. Chem.*, 1970, **35**, 3448; A. Kreutzberger, *Pharmazie*, 1970, **25**, 460; A. Kreutzberger, *Chem. Ber.*, 1966, **99**, 2237.
[18] H. Reimlinger and M. A. Peiren, *Chem. Ber.*, 1970, **103**, 3266.

series of triazolotriazines with N-4 of the triazole ring at a ring junction [as in (16)] are deshielded in comparison with the triazole protons in the isomeric series with the triazole N-1 at the ring junction [as in (17)]. If the triazolotriazine had structure (17), the triazole proton would have a chemical shift comparable to that of the corresponding proton at C-7 in the pyrazolotriazine (12). This pyrazole proton absorbs as a high-field doublet at τ 1·80 (J 2—3 Hz). The low-field triazole proton absorption at τ 0·90 in the triazolotriazine from (2) and (3) indicates that N-4 of the triazole occupies the bridgehead position.

Conclusive support for structure (16) was afforded by the identity of the triazolotriazine with the product obtained by treating benzil with 3,4-diamino-1,2,4-triazole (18) in a basic medium.[19] Any Dimroth rearrangement of the triazolotriazine (16) thus formed that is distinct from that which would lead to isomer (15) and thence to (17), would involve the highly unlikely fission of the triazine N–N bond.

EXPERIMENTAL

Benzil Mono[(aminoamidino)hydrazone] (2).—(i) A pure sample of benzil mono(aminoamidino)hydrazone nitrate [5] (prepared from diaminoguanidine nitrate [20] and benzil) was dissolved in the minimum of methanol, and the filtered solution was added to a large excess of filtered distilled ice–water containing aqueous ammonia. The white *hydrazone base*, m.p. 96—98° (with resolidification, and remelting at 171—173°) was collected and washed with filtered, distilled water (Found: N, 24·6. $C_{15}H_{15}N_5O$ requires N, 24·9%); $\nu_{max.}$ (KBr) 1650 cm^{-1} (C=O).

(ii) A solution of benzil (10·5 g) and diaminoguanidine hydroiodide [21] (10·9 g) in ethanol (100 ml) was boiled for 5 h and the dark brown solution was concentrated to 30 ml. A pale brown solid (7·5 g; m.p. 140—145°) was deposited when the concentrated solution was diluted with water (100 ml); this was not further investigated. The filtrate, when made basic with aqueous ammonia, afforded benzil mono[(aminoamidino)hydrazone] (5·0 g), identical (i.r. spectrum) with the aforementioned sample.

Benzil Mono[(aminoamidino)hydrazone] Toluene-p-*sulphonate*.—To a solution of toluene-*p*-sulphonic acid (0·35 g) in ethanol (10 ml) was added powdered benzil mono[(aminoamidino)hydrazone] (0·4 g). The resulting solution deposited crystals of the *toluene*-p-*sulphonate* (0·4 g), which formed prisms, m.p. 194—195° (from ethanol) (Found: C, 58·4; H, 5·2; N, 15·5. $C_{22}H_{23}N_5O_4S$ requires C, 58·3; H, 5·1; N, 15·4%). Basification of the salt with aqueous ammonia led to the recovery of unchanged hydrazone base.

3-*Hydrazino*-5,6-*diphenyl*-1,2,4-*triazine* (3).—(i) Benzil mono[(aminoamidino)hydrazone] (2·0 g) was boiled in ethanol (20 ml) for 1 h. The cooled solution deposited yellow needles of the hydrazine (1·8 g; m.p. 172—173°), identical (i.r. spectrum) with an authentic sample prepared from 3-chloro-5,6-diphenyl-1,2,4-triazine and hydrazine.[6]

(ii) Attempted crystallisation of benzil mono[(aminoamidino)hydrazone] from methanol, ethanol, chloroform, benzene, or chloroform–light petroleum led to formation of the same hydrazinotriazine.

(iii) Treatment of benzil mono[(aminoamidino)hydrazone] nitrate with sodium acetate according to the method of Lieber and Strojny (Preparation B),[5] followed by crystallisation from methanol, gave the same hydrazinotriazine.

6,7-*Diphenyltetrazolo*[1,5-b]-as-*triazine* (9).—(i) Benzil mono[(aminoamidino)hydrazone] (0·65 g) was ground with 2N-hydrochloric acid (20 ml) at 0° until the gum that originally formed had solidified. Sodium nitrite (0·18 g) was added in portions and the mixture was stirred at 0° (2 h). The precipitated solid (0·45 g; m.p. 70—80° with resolidification) had $\nu_{max.}$ (KBr) 2140 (N_3) and 1670 cm^{-1} (C=O). The crude solid crystallised from ethanol to afford the *tetrazolotriazine* as cream needles, m.p. 197—198° (efferv.)* (Found: C, 65·8; H, 3·9; N, 30·7. $C_{15}H_{10}N_6$ requires C, 65·7; H, 3·7; N, 30·7%). The tetrazolotriazine was recovered unchanged from boiling acetic acid or pyridine (2 h).

(ii) Diazotisation of benzil mono[(aminoamidino)hydrazone] in 20% hypophosphorous acid at 25° gave a solid, which, when crystallised from ethanol, afforded the same tetrazolotriazine (85%).

(iii) 5,6-Diphenyl-3-hydrazino-1,2,4-triazine (1·3 g) in 2N-hydrochloric acid (10 ml) was diazotised at 0° with sodium nitrite (0·4 g). The precipitated solid (1·3 g) had m.p. 85—90° (with resolidification), and a weak i.r. absorption (KBr) at 2136 cm^{-1} (N_3). Recrystallisation of the solid from ethanol gave the tetrazolotriazine, identical (i.r. spectrum) with the foregoing samples.

(iv) 3-Chloro-5,6-diphenyl-1,2,4-triazine (2·67 g) was boiled (2 h) in acetone (20 ml) containing sodium azide (1·0 g) in water (10 ml). The tetrazolotriazine (2·54 g), precipitated by the addition of excess of water, had m.p. and mixed m.p. 197—198° (efferv.).

5,6-*Diphenyl*-3-*piperidino*-1,2,4-*triazine* (1d).—The tetrazolotriazine (0·4 g) was boiled in piperidine (10 ml) for 1 h. Water was added; the precipitated *piperidinotriazine* (0·45 g) crystallised from aqueous ethanol as yellow needles, m.p. 139—140° [Found: C, 75·8; H, 6·4; N, 17·5%; M (mass spec.), 316. $C_{20}H_{20}N_4$ requires C, 75·9; H, 6·4; N, 17·7%; M, 316].

The same piperidinotriazine was obtained (72%) from 3-chloro-5,6-diphenyl-1,2,4-triazine and piperidine (1 mol. equiv.) in boiling ethanol containing sodium acetate trihydrate (1 mol. equiv.).

3-*Morpholino*-5,6-*diphenyl*-1,2,4-*triazine* (1e).—Prepared from either the tetrazolotriazine in boiling morpholine (76%), or from 3-chloro-5,6-diphenyl-1,2,4-triazine and morpholine–sodium acetate (82%), this *morpholinotriazine* crystallised as yellow prisms (from ethanol), m.p. 143—144° [Found: C, 71·8; H, 5·5; N, 17·7%; M (mass spec.), 318. $C_{19}H_{18}N_4O$ requires C, 71·7; H, 5·7; N, 17·6%; M, 318].

3-*Diethylamino*-5,6-*diphenyl*-1,2,4-*triazine* (1f).—Synthesised from the tetrazolotriazine in boiling diethylamine

* This tetrazolotriazine (9) has been referred to by Sasaki *et al.*[13a] Its physical properties (m.p. and electronic absorption spectrum) accord well with those reported in the present work. However, no analytical data were presented, and the method of preparation and literature m.p. (198°) are attributed to Takahayashi.[13b] This latter paper, however, does not mention the tetrazolotriazine (9), and it is not recorded in *Chem. Abs.*

[19] E. Hoggarth, *J. Chem. Soc.*, 1952, 4811.
[20] G. I. Keim, R. A. Henry, and G. B. L. Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 4944.
[21] F. L. Scott, D. H. O'Sullivan, and J. Reilly, *J. Appl. Chem.*, 1952, 184.

(10 h) (18%), or from 3-chloro-5,6-diphenyl-1,2,4-triazine and diethylamine (60%), the *diethylaminotriazine* crystallised from aqueous ethanol as yellow prisms, m.p. 109—110° [Found: C, 75·4; H, 6·6; N, 18·1%; *M* (mass spec.), 304. $C_{19}H_{20}N_4$ requires C, 75·0; H, 6·6; N, 18·4%; *M*, 304].

1,4-*Bis*-(5,6-*diphenyl*-1,2,4-*triazin*-3-*yl*)*piperazine* (13).—Prepared from either the tetrazolotriazine and piperazine (0·5 mol. equiv.) at 130° (1 h), or from 3-chloro-5,6-diphenyl-1,2,4-triazine and piperazine (0·5 mol. equiv.) in boiling ethanol containing sodium acetate trihydrate, this *piperazine* crystallised from dimethylformamide as yellow flakes, m.p. 313—315° [Found: C, 74·5; H, 5·1; N, 20·2%; *M* (mass spec.), 548. $C_{34}H_{28}N_8$ requires C, 74·4; H, 5·1; N, 20·4%; *M*, 548].

Benzaldehyde (5,6-*Diphenyl*-1,2,4-*triazin*-3-*yl*)*hydrazone*.—A mixture of benzaldehyde (0·23 g) and benzil mono-[(aminoamidino)hydrazone] (0·52 g) in boiling ethanol (20 ml) deposited the benzaldehyde hydrazone (0·6 g; m.p. 249—251°) when the solution was boiled (10 min). The product was identical (i.r. spectrum) with that formed by heating 5,6-diphenyl-3-hydrazino-1,2,4-triazine and benzaldehyde (1 mol. equiv.) in ethanol (lit.,[22] m.p. 252°).

5,6-*Diphenyl*-3-*triacetylhydrazino*-1,2,4-*triazine* (14).—Benzil mono[(aminoamidino)hydrazone] (1·3 g) was boiled in acetic anhydride (3 ml) for 1 h and excess of acetic anhydride was then decomposed with water. The precipitated *triacetyl derivative* (0·9 g) crystallised from ethanol as cream prisms, m.p. 143—144° (Found: C, 64·4; H, 4·9; N, 17·8. $C_{21}H_{19}N_5O_3$ requires C, 64·8; H, 4·9; N, 18·0%), $\nu_{max.}$ (KBr) 1735, 1725, and 1709 cm^{-1} (C=O), τ ($CDCl_3$) 7·58 (6H, s) and 7·21 (3H, s).

The same triacetyl derivative (85%) was formed from 3-hydrazino-5,6-diphenyl-1,2,4-triazine in boiling acetic anhydride (1 h).

3,4-*Diamino*-1,2,4-*triazole* (18) *Hydroiodide*.—A mixture of diaminoguanidine hydroiodide (10·9 g) [21] and 98—100% formic acid (2·3 g) formed a melt on a steam-bath (1 h). Crystallisation of the cooled melt from ethanol afforded the *triazole hydroiodide* (7·0 g) as needles, m.p. 164—166° (decomp.) (Found: C, 10·4; H, 2·9; N, 30·8. $C_2H_5N_5$,HI requires C, 10·6; H, 2·7; N, 30·9%).

6,7-*Diphenyltriazolo*[4,3,-b]-as-*triazine* (16).—(i) 3-Hydrazino-5,6-diphenyl-1,2,4-triazine (0·53 g) in triethyl orthoformate (5 ml) was boiled for 3 h. The yellow solution deposited a buff crystalline solid (0·5 g, 90%), m.p. 181—182°, identical with the product formed from benzil and 3,4-diamino-1,2,4-triazole base according to the method of Hoggarth (lit.,[19] m.p. 182—183°).

The same triazolotriazine was formed from the hydrazinotriazine in boiling 98—100% formic acid (2 h).

The triazolotriazine was recovered unchanged after being heated at 185° (1 h), and after being boiled (5 h) in acetic acid, pyridine, or piperidine.

(ii) Interaction of benzil mono[(aminoamidino)hydrazone] and boiling triethyl orthoformate or 98—100% formic acid afforded the same triazolotriazine (i.r. spectrum and mixed m.p.) in 90 and 95% yield respectively.

(iii) A red solution was formed when 3,4-diamino-1,2,4-triazole hydroiodide (0·57 g) and benzil (0·53 g) were boiled in piperidine (10 ml) for 1 h. The solid (95%) deposited when the cooled solution was diluted with water, was identical (i.r. spectrum) with the foregoing samples.

The same triazolotriazine (80%) was formed when boiling ethanol (10 ml) containing potassium hydroxide (0·3 g) was employed as solvent; there was no reaction, however, in the absence of the alkali.

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[22] A. Dornow, W. Abele, and H. Menzel, *Chem. Ber.*, 1964, **97**, 2179.