The Chemistry of Polyazaheterocyclic Compounds. Part VIII.[1] Coupling Reactions of 1,2,4-Triazole-5-diazonium Nitrate with Active Methylene Compounds. A New General Route to [1,2,4]Triazolo[5,1-*c*][1,2,4]triazine Derivatives

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1,2.4-Triazole-5-diazonium nitrate couples with a variety of active methylene compounds (diethyl malonate, ethyl benzoylacetate, acetylacetone, benzoylacetone, dibenzoylmethane, and benzoylacetonitrile) at room temperature in the presence of sodium acetate to afford 1.2.4-triazol-5-ylhydrazones, which are smoothly converted in warm aqueous ethanolic sodium acetate or glacial acetic acid, in high yield, into the corresponding [1,2.4]triazolo[5.1-*c*]-[1.2,4]triazine derivatives. In the cases of ethyl acetoacetate and cyanoacetamide the derived hydrazones were unstable and underwent spontaneous cyclisation even at room temperature, affording the corresponding triazolotriazines.

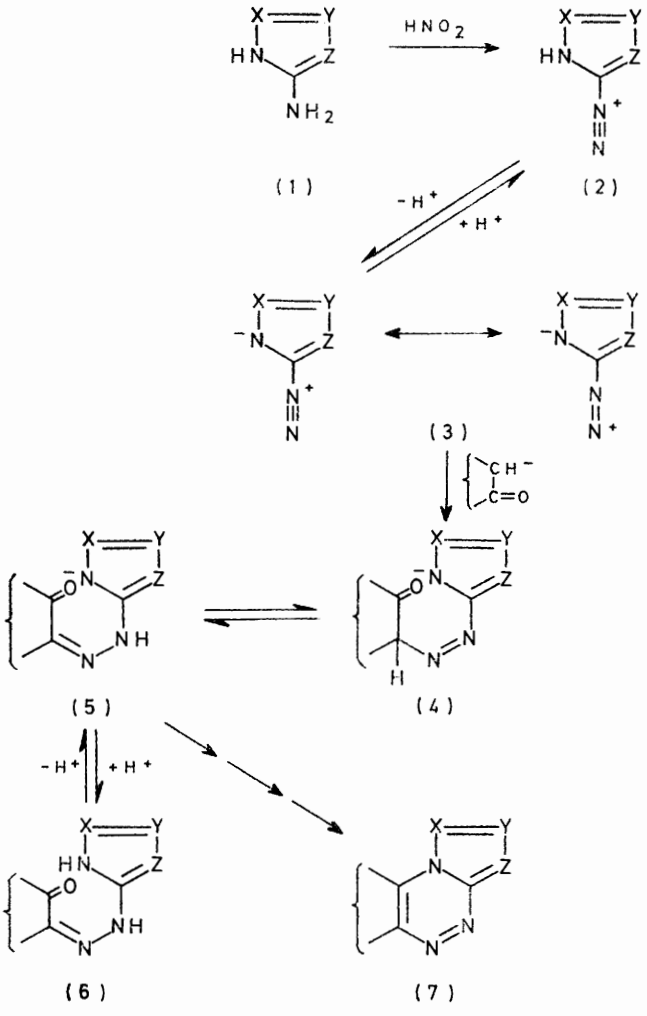
DESPITE their ready accessibility by diazotisation of the corresponding amino-heterocycles, the chemical reactivity of five-membered heterocyclic diazonium salts has, in comparison with their benzenoid counterparts, been little investigated.[2] Diazonium salts (2) derived from 1*H*-aminoazoles (1) are of particular interest as sources of 1,4-dipoles of the type (3). Thus, diazonium salts (2a and b) derived from 3-amino-2*H*-pyrazoles (1a) and 5-amino-1*H*-1,2,3-triazoles (1b) are converted in neutral or weakly basic solution into the relatively stable diazonium betaines (3a)[3] and (3b).[4] 1,4-Dipoles (3) may also be invoked as reactive intermediates in the coupling reactions of 2*H*-indazole-3-diazonium salts[5] and pyrazole-5-diazonium salts[3,6,7] with active methylene compounds[5,6] and phenols[3,7] to afford hydrazones convertible by cyclisation into indazolo[3,2-*c*][1,2,4]triazines and pyrazolo[5,1-*c*][1,2,4]triazines, respectively [*cf.* Scheme; (3) ⟶ (4) ⟶ (5) ⇌ (6) ⟶ (7)]. As part of a general investigation of the chemistry of diazonium salts of the type (2) and the related 1,4-dipoles (3) we recently described[8] a general synthesis of the previously unknown 1,2,3-triazolo[5,1-*c*][1,2,4]triazine ring system (7b) based on the coupling reactions of 4-phenyl-1,2,3-triazole-5-diazonium chloride (2; X = Y = N, Z = CPh) with active methylene compounds. Analogous coupling reactions of 1,2,4-triazole-5-diazonium nitrate are now shown to provide a new, general synthesis of otherwise not readily accessible [1,2,4]triazolo-[5,1-*c*][1,2,4]triazine derivatives (7; X = Z = N, Y = CH).

The ready replacement of the diazonium group in 1,2,4-triazole-5-diazonium salts by chloride ion[9,10] precluded the study of the reactions of 1,2,4-triazole-5-diazonium chloride with active methylene compounds. Coupling reactions were therefore carried out *in situ* by using solutions in dilute nitric acid of the relatively stable[10] 1,2,4-triazole-5-diazonium nitrate. Previous work had shown[11] that 3-alkyl-1,2,4-triazole-5-diazonium nitrates coupled with acetylacetone and ethyl acetoacetate to give products which were not characterised but gave correct analytical data for the corresponding 1,2,4-triazol-5-ylhydrazones. In the present studies, a buffered solution of 1,2,4-triazole-5-diazonium nitrate coupled smoothly and in high yield with diethyl malonate at room temperature to give a readily separated mixture of two acidic products (A) and (B), the former in major amount. The product (A) gave analytical data consistent with the expected hydrazone (8a). However, its i.r. spectrum showed multiple NH absorption at 3 250—2 700 cm^{-1} and carbonyl absorption at 1 720 and 1 690 cm^{-1}, consistent with the presence of two different carbonyl groups. These spectroscopic properties can be explained in terms of an internally hydrogen-bonded structure (9), which also accounts for the ^1H n.m.r. spectrum. This shows a broad one-proton singlet at τ 1.69 assigned to H-3 of the triazole ring and a four-proton quintet and a six-proton overlapping double triplet centred at τ 5.75 and 8.75 demonstrating the presence of a bonded and an unbonded ethoxycarbonyl group. The absence of any other CH absorption in the ^1H n.m.r. spectrum of (A) excludes the presence of the azo-tautomer (10). The attempted demonstration of free triazole NH in the structure (8a) by acetylation[12] led to decomposition of the substrate.

The acidic product (B), $C_7H_7N_5O_3$, was also obtained in excellent yield when the hydrazone (8a) was heated under reflux with aqueous ethanolic sodium acetate or

[1] Part VII, D. R. Sutherland and G. Tennant, *J.C.S. Perkin I*, 1974, 534.
[2] J. M. Tedder, *Adv. Heterocyclic Chem.*, 1967, **8**, 1; R. N. Butler, *Chem. Rev.*, 1975, **75**, 241.
[3] H. Reimlinger, A. van Overstraeten, and H. G. Viehe, *Chem. Ber.*, 1961, **94**, 1036.
[4] Y. F. Shealy, R. F. Struck, L. B. Holum, and J. A. Montgomery, *J. Org. Chem.*, 1961, **26**, 2396; M. Regitz, *Angew. Chem. Internat. Edn.*, 1967, **6**, 747; H. Mackie and G. Tennant, unpublished work.
[5] G. R. Bedford, F. C. Cooper, M. W. Partridge, and M. F. G. Stevens, *J. Chem. Soc.*, 1963, 5901; *cf.* also D. Fortuna, B. Stanovnik, and M. Tisler, *J. Org. Chem.*, 1974, **39**, 1833; R. Allmann, T. Debaerdemaeker, W. Grahn, and C. Reichardt, *Chem. Ber.*, 1974, **107**, 1555.
[6] M. W. Partridge and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1966, 1127; *cf.* also J. Slouka, V. Bekarek, and J. Kubata, *Monatsh.*, 1974, **105**, 535.
[7] H. Reimlinger and A. van Overstraeten, *Chem. Ber.*, 1966, **99**, 3350.
[8] H. Mackie and G. Tennant, *Tetrahedron Letters*, 1972, 4719.
[9] J. Thiele and W. Manchot, *Annalen*, 1898, **303**, 33.
[10] G. T. Morgan and J. Reilly, *J. Chem. Soc.*, 1916, **109**, 155.
[11] J. Reilly and P. J. Drumm, *J. Chem. Soc.*, 1926, 1729.
[12] D. R. Sutherland, G. Tennant, and R. J. S. Vevers, *J.C.S. Perkin I*, 1973, 943.

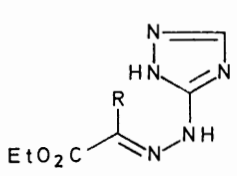
glacial acetic acid, or when an aqueous ethanolic mixture of 1,2,4-triazole-5-diazonium nitrate and diethyl malonate buffered with sodium acetate was heated under reflux. The i.r. spectrum of (B) showed bands at 3 100—2 700 and 1 695, and 1 740 cm^{-1} consistent with a cyclic amide structure containing an ethoxycarbonyl group. The presence of the latter substituent was verified by alkaline hydrolysis of (B) to a heavily hydrated carboxylic



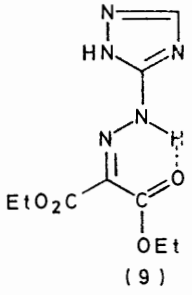
a; X = N, Y = Z = CR
b; X = Y = N, Z = CR

SCHEME

acid, which was also the product when an aqueous ethanolic mixture of 1,2,4-triazole-5-diazonium nitrate and diethyl malonate containing sodium carbonate was heated under reflux. The [1,2,4]triazolo[5,1-*c*][1,2,4]-triazine structures (11b and c) for (B) and the derived carboxylic acid are in accord with the position (τ 1.56—1.60) of the resonances of the triazole CH (*i.e.* H-2) (Table 3), at higher field than the triazole CH resonances (τ *ca.* 1.00) anticipated [13] for the alternative [1,2,4]-triazolo[3,4-*c*][1,2,4] triazine formulations (13b and c) and the structurally less likely [4,3-*b*]-fused frameworks (14b and c). After the present studies were complete, Daunis and Follet [14] reported a synthesis of the ester (11b) based on the orthodox condensation of ethyl



(8) R
a; CO_2Et
b; COMe
c; COPh



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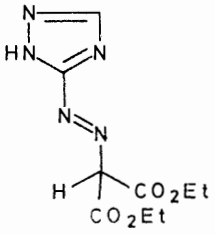
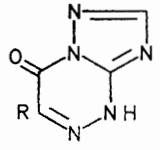
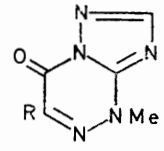


(10)

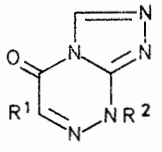
3-hydrazino-2,5-dihydro-5-oxo-1,2,4-triazine-6-carboxylate with formic acid. However, though identical in terms of their ^1H n.m.r. absorption (*cf.* Table 3 and ref. 14), the ester and the corresponding carboxylic acid



(11) R
a; H
b; CO_2Et
c; CO_2H
d; $CO{\cdot}NH_2$
e; COPh



(12) R
a; H
b; $CO{\cdot}NH_2$
c; COPh

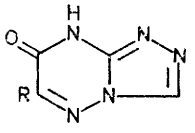


(13) R^1 R^2
a; H H
b; CO_2Et H
c; CO_2H H
d; H Me

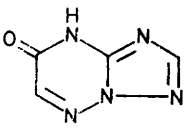
described [14] by Daunis and Follet differ markedly in m.p. from the products (11b and c) obtained in the

[13] J. Daunis, R. Jacquier, and P. Viallefont, *Bull. Soc. chim. France*, 1969, 2492.
[14] J. Daunis and M. Follet, *Bull. Soc. chim. France*, 1975, 857.

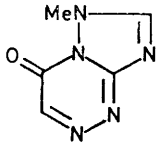
present work. In addition, the carboxylic acid obtained by the hydrolysis of (B) showed a u.v. absorption which is similar in wavelength but markedly more intense than



(14) R
a; H
b; CO_2Et
c; CO_2H



(15) R
a; H
b; CO_2Et
c; CO_2H



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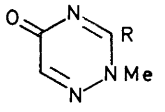
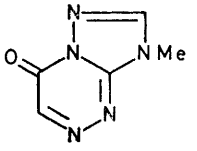


(18) R
a; SMe
b; $NH{\cdot}NH_2$
c; NH·N:CHPh



(17)

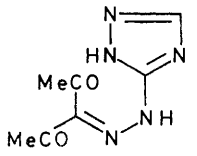
that of the acid reported [14] by Daunis and Follet. Despite these discrepancies, the structures (11b and c) for (B) and the derived carboxylic acid are firmly established by the following evidence which excludes the isomeric structures (13b and c) as well as the only remotely possible [4,3-*b*]-fused and [2,3-*b*]-fused alternatives (14b and c) and (15b and c). The anhydrous acid (11c) was readily decarboxylated by heating *in vacuo* to afford a product having m.p. and u.v. and ^1H n.m.r. spectra identical with those described [13] for a compound formulated as [1,2,4]triazolo[5,1-*c*][1,2,4]triazin-7(4*H*)-one (11a). This structure for the decarboxylated compound was rigorously confirmed by methylation, which yielded a readily separated mixture of an *N*-methyl derivative, m.p. 174°, and an isomer whose precise structure has not yet been determined but may be tentatively formulated as either the 1-*N*-methyl derivative (16) or the 3-*N*-methyl derivative (17). The 4-*N*-methyl structure (12a) for the *N*-methyl derivative, m.p. 174°, was firmly established by its unambiguous synthesis. This was accomplished by reaction of the thiomethyltriazinone (18a) of established [15] orientation, with hydrazine to yield the hydrazinotriazinone (18b), characterised as the benzylidene derivative (18c). Prolonged heating of the hydrazinotriazinone (18b) with formic acid afforded a single product, identical with the compound of m.p. 174°. On the other hand, brief heating of the hydrazinotriazinone (18b) with formic acid gave an isomer, m.p. 166°, which was convertible in turn into the compound of m.p. 174° by further heating in formic acid or with aqueous ethanolic sodium acetate. The formation of both these compounds from the hydrazinotriazinone (18b), in which N-2 is blocked by a methyl substituent, rules out structures based on the nuclei (14a) and (15a). Conversely, the ready rearrangement [13] of the compound of m.p. 166° to the isomer, m.p. 174°, and the high- and low-field positions, respectively, of the triazole CH resonances (Table 3) allow the assignment of the [1,2,4]triazolo[5,1-*c*][1,2,4]triazine structure (12a) to the compound of m.p. 174° and, correspondingly, the [1,2,4]triazolo[3,4-*c*][1,2,4]triazine structure (13d) to the isomer of m.p. 166°. The close similarity in the u.v. spectra (Table 1) and the n.m.r. absorptions of H-2 and H-6 in the *N*-methyl derivative (12a) and the parent decarboxylated compound confirms the triazolotriazinone structure (11a) for the latter. The structures assigned to the ester (11b) and the derived carboxylic acid (11c) follow from the close correspondence of their H-2 resonances with those of the triazolotriazinones (11a) and (12a) and marked dissimilarity with that of 4-methyl-[1,2,4]triazolo[3,4-*c*][1,2,4]triazine (13d) (*cf.* Table 3). The reasons for the differing properties of the ester (11b) and the acid (11c) reported in the present studies and the corresponding products described by Daunis and Follet are not clear. The propensity for these and related [1,2,4]triazolo[5,1-*c*][1,2,4]triazines (see later) to undergo solvation might explain the differing m.p.s. On the other hand, the enhanced u.v. absorption intensity in comparison with the parent triazolotriazinone (11a) [13] found in the present studies for the acid (11c) parallels that of the related structures (11b and e) (Table 1) bearing a carbonyl substituent at C-6 and is fully consistent with the hyperchromic effect anticipated [16] in going from an αβ-unsaturated carbonyl chromophore to a cross-conjugated enedione structure.

1,2,4-Triazole-5-diazonium nitrate also coupled readily at room temperature in the presence of sodium acetate with acetylacetone and benzoylacetone to afford high yields of products which gave analytical and mass spectral data and showed i.r. and ^1H n.m.r. spectra in accord with their formulation as the expected hydrazones (19) and (20a). Heating the hydrazones (19) and (20a) under reflux in glacial acetic acid [and in the case of the compound (19) with aqueous ethanolic sodium acetate] gave high yields of amorphous products which were also formed directly by heating mixtures of 1,2,4-triazole-5-diazonium nitrate and acetylacetone or benzoylacetone in aqueous ethanolic sodium acetate. Despite their ill defined character in comparison with the structurally closely related ketone (21f) (discussed later), these amorphous products gave mass spectra consistent with their formulation as the [1,2,4]triazolo[5,1-*c*][1,2,4]-triazines (21a and b). On the other hand they analysed

[15] J. Gut, M. Prystas, J. Jonas, and F. Sorm, *Coll. Czech. Chem. Comm.*, 1961, **26**, 974.

[16] E. S. Stern and C. J. Timmons, ' Introduction to Electronic Absorption Spectroscopy in Organic Chemistry,' 3rd edn., Arnold, London, 1970, pp. 96—99.

consistently as hemihydrates of these structures, thus accounting for the hydroxy as well as carbonyl absorption present in their i.r. spectra and also possibly for the featureless ^{1}H n.m.r. spectra which they exhibit. Attempts to obtain the anhydrous [1,2,4]triazolo[5,1-*c*]-[1,2,4]triazines (21a and b) were unsuccessful. The



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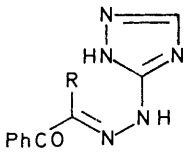
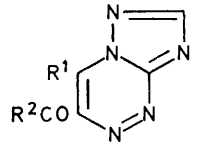
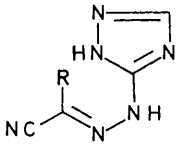


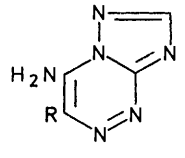
(20) R
a; COMe
b; COPh



(21) R^1 R^2
a; Me Me
b; Me Ph
c; Me OEt
d; Me OH
e; Ph OEt
f; Ph Ph



(22) R
a; COPh
b; CO·NH$_2$



(23) R
a; COPh
b; CO·NH$_2$

structure (21b) rather than the alternative formulation (21; R^1 = Ph, R^2 = Me), for the triazolotriazine derived from benzoylacetone is consistent with the absorption frequency of the ketonic carbonyl group (1 660 cm^{-1}) which is akin to that (1 670 cm^{-1}) of the phenyl ketone (21f) (see later) and significantly lower than that (1 690 cm^{-1}) of the acetyltriazolotriazine (21a). Unlike acetylacetone and benzoylacetone, ethyl acetoacetate did not yield the corresponding hydrazone (8b) on reaction with 1,2,4-triazole-5-diazonium nitrate at room temperature in the presence of sodium acetate. Instead the amorphous product, which was also formed in high yield when a mixture of 1,2,4-triazole-5-diazonium nitrate and ethyl acetoacetate in aqueous ethanolic sodium acetate was heated under reflux, is formulated on the basis of analytical and spectral data as the hemihydrate of ethyl-7-methyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazine-6-carboxylate (21c). In further support of this structure assignment, alkaline hydrolysis of the amorphous product from ethyl acetoacetate yielded the corresponding carboxylic acid (21d).

In contrast to ethyl acetoacetate, ethyl benzoylacetate coupled with 1,2,4-triazole-5-diazonium nitrate at room temperature in the presence of sodium acetate to give the expected hydrazone (8c) in high yield. The multiple ethoxycarbonyl absorption in the ^{1}H n.m.r. spectrum of this product can be attributed to the presence of both possible geometrically isomeric forms of the structure (8c). Despite the presence of both isomers, however, cyclisation of the hydrazone (8c) in hot glacial acetic acid, or *in situ* in hot aqueous ethanolic sodium acetate, afforded a single product in high yield. The spectral properties of this product in conjunction with its ready conversion into an *N*-methyl derivative (12c) and its alternative formation by hydrolysis of the amino-ketone (23a) (see later), firmly establish its identity as the triazolotriazinone (11e). The product (21e) of alternative cyclisation *via* the benzoyl group in the hydrazone (8c) was not detected, thus demonstrating preferential cyclisation *via* the ethoxycarbonyl group. The reluctance of a benzoyl group to participate in cyclisative condensation was also encountered in the hydrazone (20b) derived from dibenzoylmethane which, in contrast to the structurally closely related hydrazone (19), was stable to heating under reflux in aqueous ethanolic sodium acetate. However, cyclisation of the hydrazone (20b) occurred readily on heating with glacial acetic acid to give the anticipated [1,2,4]triazolo[5,1-*c*][1,2,4]triazine (21f) in high yield.

The relative inertness of the benzoyl group was also manifest in the exclusive formation of the amino-ketone (23a) by acetic acid- or sodium acetate-catalysed cyclisation of the hydrazone (22a), formed in good yield by condensation of 1,2,4-triazole-5-diazonium nitrate with benzoylacetonitrile. The structure of the amino-ketone (23a) follows from the presence of i.r. bands at 3 400 and 3 150, and 1 640 cm^{-1}, attributable respectively to a primary amino-group and a benzoyl group, and from its hydrolytic conversion [1] in aqueous acid into the triazolotriazinone (11e) obtained before. Like the carbonyl compounds (21a—c) (see before) and the amino-amide (23b) (see later), the amino-ketone (23a) showed a tendency to form solvates with protic solvents such as ethanol, which reverted to the free compound on heating *in vacuo*. Attempts to diazotise the amino-group in the compound (23a) were unsuccessful. The condensation of 1,2,4-triazole-5-diazonium nitrate with cyanoacetamide in buffered solution at room temperature afforded (together with resinous material) a product whose spectroscopic properties are consistent with the hydrazone structure (22b). However, this product was unstable and on crystallisation gave the aminotriazolotriazinecarboxamide (23b), which was also formed by cyclising the hydrazone (22b) *in situ*. In accord with the assigned structure, acidic hydrolysis of the aminotriazolotriazine (23b) afforded the triazolotriazinone (11d), identical with the product of the amination of the ester (11b) of established structure.

Hitherto, syntheses of [1,2,4]triazolo[5,1-*c*][1,2,4]-triazine derivatives have been based principally on cyclis-

ative condensation reactions with 3-hydrazino-[13,17] or 3,4-diamino-[18] 1,2,4-triazines. However, the flexibility and generality of these methods are impaired by the poor accessibility of the requisite 1,2,4-triazine substrates and by a degree of ambiguity[13,14] in the mode of ultimate ring closure. The present studies demonstrate that the coupling of readily accessible 1,2,4-triazole-5-diazonium salts with active methylene compounds and subsequent cyclisation of the resulting hydrazones, either after isolation or *in situ*, provides a highly flexible, general route to [1,2,4]triazolo[5,1-*c*][1,2,4]triazines containing a variety of functional groups at C-6 and C-7.

EXPERIMENTAL

I.r. and u.v. spectra were recorded for Nujol suspensions and ethanolic solutions, respectively, with Unicam SP 200 and SP 800 instruments. U.v. data for [1,2,4]triazolo-[5,1-*c*][1,2,4]triazines are collected in Table 1. ^{1}H N.m.r. spectra were measured at 100 MHz for solutions in deuteriochloroform or [$^2H_6$]dimethyl sulphoxide, at 28 °C, with an A.E.I. MS 902 spectrometer. Light petroleum had b.p. 60—80°. Silica for chromatography was Fisons 100—200 mesh. Organic extracts were dried ($MgSO_4$) prior to evaporation under reduced pressure.

TABLE 1

U.v. absorption of [1,2,4]triazolo[5,1-*c*][1,2,4]triazines

Compd.	$\lambda_{max.}$/nm	log $\varepsilon_{max.}$
(11a)	213, 241, 246sh, 269sh, 298	3.83, 3.55, 3.53, 3.53, 3.81
(11b)	208, 220sh, 261sh, 273, 318	4.06, 3.93, 3.64, 3.68, 4.00
(11c)	216, 242inf, 280sh, 312	4.15, 3.62, 3.71, 3.97
(11e)	210, 257, 305	4.20, 4.06, 3.98
(12a)	212, 244, 250sh, 300	3.80, 3.70, 3.62, 3.93
(12c)	209, 259, 312	4.21, 4.08, 4.05
(13d)	217, 238, 319	3.92, 3.80, 3.85
(16)/(17)	221, 258, 268sh, 342	4.20, 3.49, 3.33, 3.94
(21a) [a]	208, 319	3.67, 3.78
(21f)	213, 258, 331	4.31, 4.29, 3.91
(23a)	216, 243sh, 300, 331	4.22, 3.86, 4.07, 4.15

[a] Hemihydrate.

TABLE 2

^{1}H N.m.r. signals (τ values) of 1,2,4-triazol-5-yl-hydrazones [a]

Compd.	H-3	ArH	Others	
(8a)	1.69		5.72 [b,c] 8.75 [b,d]	
(8c)	2.27		6.01 [b,e] 8.99 [b,f]	2.00 [g]
(19)	2.17		7.65 [h] 7.91 [h]	2.84 [g]
(20a)	2.11	2.12—2.72 (m)	7.84 [h]	
(20b) [j]	2.21	2.23—2.77 (m) [k]		
(22a)	2.14	2.59 [i]	1.34 [g]	
(22a) [l]	2.09	2.55 [i]	1.29 [g]	6.54 (q) [b] 8.94 (t) [b]

[a] Spectra taken at 100 MHz on a Varian HA 100 instrument; solutions in [$^2H_6$]dimethyl sulphoxide at 28 °C with tetramethylsilane as internal standard. Signals were sharp singlets unless otherwise designated. [b] OEt. [c] 4 H, quintet. [d] 3 H, overlapping double triplet. [e] 4 H, overlapping double quartet. [f] 6 H, broad triplet. [g] NH, broad singlet. [h] COMe. [i] 5 H. [j] Spectrum run in $CDCl_3$. [k] 10 H. [l] Ethanol solvate.

tetramethylsilane as internal standard with a Varian HA-100 instrument. ^{1}H N.m.r. data for 1,2,4-triazol-5-ylhydrazones and [1,2,4]triazolo[5,1-*c*][1,2,4]triazines are collected in Tables 2 and 3. Mass spectra were measured at 70 eV with

[17] A. Dornow, H. Menzel, and P. Marx, *Chem. Ber.*, 1964, **97**, 2185.

TABLE 3

^{1}H N.m.r. signals (τ values) of [1,2,4]triazolo[1,2,4]-triazines [a]

Compd.	H-2	ArH	Others
(11a)	1.64		2.20 [b]
(11b)	1.56		5.64 (q) [c] 8.64 (t) [c]
(11c)	1.60		
(11d)	1.59		2.15 [d]
(11e)	1.50	1.87—2.09 (m) [e] 2.15—2.53 (m) [f]	
(12a)	1.59		2.16,[b] 6.01 [g]
(12b)	1.52		2.02,[d] 5.95 [g]
(12c)	1.48	1.86—2.04 (m) [e] 2.22—2.54 (m) [f]	5.96 [g]
(13d)			0.68,[h] 2.39,[b] 6.02 [g]
(16)/(17)	1.47 [i]		1.50,[i] 5.70 [g]
(21f)	0.90	1.90—2.66 [j]	
(23a)	1.20	1.96—2.11 (m) [c] 2.30—2.46 (m) [f]	0.36 [d]
(23a) [k]	1.19	1.93—2.15 (m) [e] 2.29—2.55 (m) [f]	0.37,[d] 6.67 (q) [c] 8.95 (t) [c]
(23b)	1.28		0.47,[l] 0.59,[l] 1.48,[l] 2.20 [l]

[a] As Table 2. [b] H-6. [c] OEt, J 7 Hz. [d] NH_2, broad singlet. [e] 2 H. [f] 3 H. [g] NMe. [h] H-1. [i] H-2 or H-6. [j] 10 H. [k] Ethanol solvate. [l] NH, broad singlet.

1,2,4-*Triazol-5-ylhydrazones*.—A stirred solution of 5-amino-1,2,4-triazole (1.3 g, 0.015 mol) in concentrated nitric acid (*d* 1.42; 1.5 ml) and water (3.5 ml) was cooled to 0 °C and treated dropwise with sodium nitrite (0.9 g) in the minimum volume of water. After stirring at 0 °C for 10 min, the pale yellow diazonium solution was added dropwise with stirring at 0—10 °C to a solution of the active methylene compound (0.015 mol) and anhydrous sodium acetate (1.6 g) in water (4.0 ml) and ethanol (10.0 ml). The mixture was stirred at room temperature for 2 h and then worked up as described for individual reactions.

(*a*) The mixture from diethyl malonate was filtered to afford the *hydrazone* (8a) (1.9 g), which formed yellow prisms, m.p. 140° (from ethanol), $\nu_{max.}$ 3 250, 3 100, and 2 700br (NH), and 1 720 and 1 690 cm^{-1} (CO) (Found: C, 42.5; H, 4.9; N, 27.2%; M^+, 255. $C_9H_{13}N_5O_4$ requires C, 42.4; H, 5.1; N, 27.5%; *M*, 255). The aqueous ethanolic mother liquor was concentrated, acidified (dilute aqueous sulphuric acid), and extracted with chloroform to give the triazolotriazinone (11b) (0.4 g), m.p. 198—203° (from ethanol), identical (mixed m.p. and i.r. spectrum) with a sample prepared later.

(*b*) Acetylacetone afforded the insoluble *hydrazone* (19) (1.8 g), which formed colourless prisms, m.p. 158° (from ethanol), $\nu_{max.}$ 3 350 and 3 100—2 700br (NH), and 1 680 cm^{-1} (CO), $\lambda_{max.}$ 207, 230sh, and 306 nm (log ε 3.89, 3.65, and 3.95) (Found: C, 43.3; H, 4.6; N, 36.0%; M^+, 195. $C_7H_9N_5O_2$ requires C, 43.1; H, 4.6; N, 35.9%; *M*, 195).

Concentration of the aqueous ethanolic mother liquor and extraction with chloroform yielded a gummy solid which was triturated with ether to afford the hemihydrate of the triazolotriazine (21a) (0.27 g), m.p. 196° (from ethanol),

[18] A. Dornow, H. Menzel, and P. Marx, *Chem. Ber.*, 1964, **97**, 2173.

identical (m.p. and i.r. spectrum) with a sample obtained later.

(*c*) The mixture from benzoylacetone (containing an insoluble solid) was evaporated and treated with water. The insoluble solid was extracted with hot light petroleum to remove benzoylacetone (0.5 g) and crystallised to give the *hydrazone* (20a) as yellow prisms (3.0 g), m.p. 137° (from ethyl acetate), $\nu_{max.}$ 3 300 and 3 100—2 700br (NH), and 1 640 and 1 610 cm^{-1} (CO) (Found: C, 55.9; H, 4.6; N, 27.4%; M^+, 257. $C_{12}H_{11}N_5O_2$ requires C, 56.0; H, 4.3; N, 27.2%; *M*, 257).

(*d*) Ethyl benzoylacetate yielded an insoluble solid which was combined with a second crop isolated by extracting the concentrated aqueous ethanolic mother liquor with chloroform and triturating the oil obtained with ether to remove ethyl benzoylacetate (0.56 g). Crystallisation of the crude solid gave the pure *hydrazone* (8c) (3.0 g) as a mixture of geometrical isomers, m.p. 139—144° (from ethyl acetate), $\nu_{max.}$ 3 400 and 3 100—2 700br (NH), and 1 700 and 1 620 cm^{-1} (CO) (Found: C, 54.6; H, 4.5; N, 24.4%; M^+, 287. $C_{13}H_{13}N_5O_3$ requires C, 54.4; H, 4.5; N, 24.4%; *M*, 287).

(*e*) The mixture from dibenzoylmethane (containing an insoluble solid) was concentrated and the resulting solid was heated under reflux with light petroleum to remove dibenzoylmethane (1.6 g), and crystallised to afford the hydrazone (20b) (1.7 g).

Alternatively, after being stirred at room temperature for 1 h, the mixture from dibenzoylmethane was heated under reflux for 1 h and worked up as described before to give dibenzoylmethane (1.6 g) and the *hydrazone* (20b) (2.0 g), which formed colourless plates, m.p. 184° (from ethanol–water), $\nu_{max.}$ 3 300 and 3 100—2 700br (NH) and 1 650 cm^{-1} (CO) (Found: C, 63.8; H, 4.2; N, 21.9%; M^+, 319. $C_{17}H_{13}N_5O_2$ requires C, 63.9; H, 4.1; N, 21.9%; *M*, 319).

(*f*) The solid obtained by concentrating the mixture from benzoylacetonitrile was washed with benzene to remove benzoylacetonitrile (1.1 g) and crystallised from ethanol to yield the ethanol solvate of the hydrazone (22a), $\nu_{max.}$ 3 300 and 3 200—2 700br (NH, OH), 2 250w (CN), and 1 580 cm^{-1}, which was heated *in vacuo* at 80 °C for 17 h to afford the free *hydrazone* (22a) (1.0 g), cream prisms, m.p. 168°, $\nu_{max.}$ 3 200—2 700br (NH), 2 200w (CN), and 1 620 cm^{-1} (CO) (Found: C, 55.0; H, 3.4; N, 35.0%; M^+, 240. $C_{11}H_8N_6O$ requires C, 55.0; H, 3.3; N, 35.0%; *M*, 240).

[1,2,4]*Triazolo*[5,1-*c*][1,2,4]*triazines*.—*Method* (*A*). A mixture of 1,2,4-triazole-5-diazonium nitrate (0.015 mol), the active methylene compound (0.015 mol), and anhydrous sodium acetate (1.6 g) in water (4.0 ml) and ethanol (10.0 ml) prepared as described before, was stirred at room temperature for 1 h, then heated under reflux for 1 h, and worked up as described for individual reactions.

(*a*) The cooled mixture from diethyl malonate deposited an insoluble salt which was combined with a further crop obtained by concentrating the aqueous ethanolic mother liquor, and stirred with dilute aqueous hydrochloric acid to yield *ethyl 4,7-dihydro-7-oxo*[1,2,4]*triazolo*[5,1-c][1,2,4]-*triazine-6-carboxylate* (11b) as orange prisms (1.5 g), m.p. 204° (from ethanol) (lit.,[14] 186°), $\nu_{max.}$ 3 100—2 700br (NH), and 1 740 and 1 695 (CO) cm^{-1} (Found: C, 40.1; H, 3.3; N, 33.7%; M^+, 209. $C_7H_7N_5O_3$ requires C, 40.2; H, 3.4; N, 33.5%; *M*, 209).

(*b*) Acetylacetone yielded an insoluble solid more of which was isolated by concentrating the aqueous ethanolic mother liquor and acidifying with dilute aqueous sulphuric acid. Crystallisation of the crude product gave the hemihydrate of the *triazolotriazine* (21a) as an amorphous cream powder (2.0 g), m.p. 196° (from ethanol), $\nu_{max.}$ 3 400—2 700br (OH) and 1690 cm^{-1} (CO) (Found: C, 45.4; H, 4.2; N, 37.1. $C_7H_7N_5O,0.5H_2O$ requires C, 45.2; H, 4.3; N, 37.6%), M^+ 177.

(*c*) The mixture from benzoylacetone was evaporated under reduced pressure, and treated with chloroform and water. The insoluble solid was combined with solid material obtained by triturating the oil from the chloroform extract with light petroleum to remove benzoylacetone (0.3 g), and crystallised to afford the hemihydrate of the *ketone* (21b) as an amorphous, light yellow powder (1.4 g), m.p. 157° (from ethanol–light petroleum), $\nu_{max.}$ 3 400—2 700br (OH) and 1 660 cm^{-1} (CO) (Found: C, 58.3; H, 3.9; N, 28.5. $C_{12}H_9N_5O,0.5H_2O$ requires C, 58.1; H, 4.0; N, 28.2%), M^+ 239.

(*d*) The mixture from ethyl benzoylacetate was evaporated under reduced pressure, treated with water and chloroform, and filtered to give an insoluble salt which was combined with the aqueous phase and acidified (dilute aqueous sulphuric acid) to yield the *triazolotriazinone* (11e) (1.8 g), which formed colourless needles, m.p. 255° (from glacial acetic acid), $\nu_{max.}$ 3 300—3 100br (NH), and 1 720 and 1 660 cm^{-1} (CO) (Found: C, 54.6; H, 3.0; N, 29.3%; M^+, 241. $C_{11}H_7N_5O_2$ requires C, 54.8; H, 2.9; N, 29.0%; *M*, 241).

(*e*) The cooled mixture from benzoylacetonitrile deposited the ethanol solvate of the aminotriazolotriazine (23a), $\nu_{max.}$ 3 350 and 3 200—2 700br (NH, OH), and 1 660 (CO) cm^{-1}, which was heated *in vacuo* at 80° for 4 h to afford the free *aminotriazolotriazine* (23a) as colourless plates (2.1 g), m.p. 224° (from benzene–glacial acetic acid), $\nu_{max.}$ 3400w and 3 150 (NH), 1 640 (CO), and 1 620 cm^{-1} (NH def.) (Found: C, 55.3; H, 3.5; N, 35.4%; M^+, 240. $C_{11}H_8N_6O$ requires C, 55.0; H, 3.3; N, 35.0%; *M*, 240).

(*f*) The cooled mixture from cyanoacetamide (containing a solid) was concentrated to *ca.* 10 ml. The resulting crude solid (1.5 g) was boiled with water leaving a red insoluble resin. Concentration of the aqueous extract gave the hemihydrate of the triazolotriazinecarboxamide (23b) (0.84 g), m.p. >220° (decomp.) (from water), identical (m.p. and i.r. spectrum) with a sample prepared later.

Method (*B*). (*a*) The hydrazone (20b) (1.3 g, 0.004 mol) was heated under reflux with glacial acetic acid (20.0 ml) for 2 h. The mixture was evaporated and the resulting solid was washed with ether and crystallised from benzene with hot filtration to remove some insoluble material, to afford the *phenyl ketone* (21f) as colourless plates (0.84 g), m.p. 194°, $\nu_{max.}$ 1 670 (CO) cm^{-1} (Found: C, 68.2; H, 3.7; N, 23.4%; M^+, 301. $C_{17}H_{11}N_5O$ requires C, 67.8; H, 3.7; N, 23.3%; *M*, 301).

(*b*) The hydrazones (8a and c), (19), (20a), and (22a) (0.002 mol) were heated under reflux in glacial acetic acid (10.0 ml) for 2 h, and the mixtures were worked up as described in (*a*) to afford the triazolotriazines (11b and e), (21a and b) (hemihydrates), and (23a) (60—100%), identical (m.p. and i.r. spectrum) with samples prepared before.

Method (*C*). Solutions of the hydrazones (8a) and (19) (0.015 mol) in water (10.0 ml) and ethanol (25.0 ml) were heated under reflux with anhydrous sodium acetate (1.2 g) for 1 h.

(*a*) The mixture from the hydrazone (8a) gave an insoluble salt which was augmented with material obtained by concentrating the aqueous ethanolic filtrate, and acidified

(dilute aqueous hydrochloric acid) to give the triazolotriazinone (11b) (2.2 g), m.p. 204° (from ethanol), identical (mixed m.p. and i.r. spectrum) with a sample prepared before.

(*b*) The solid obtained by evaporating the mixture from the hydrazone (19) was treated with a little water and crystallised from ethanol to give the hemihydrate of the triazolotriazine (21a) (2.6 g), m.p. 196°, identical (mixed m.p. and i.r. spectrum) with a sample prepared before.

4,7-*Dihydro*-7-*oxo*-1,2,4-*triazolo*[5,1-c][1,2,4]*triazine*-6-*carboxylic Acid* (11c).—(*a*) A solution of 1,2,4-triazole-5-diazonium nitrate in aqueous nitric acid prepared from 5-amino-1,2,4-triazole (5.0 g, 0.06 mol) as described before, was added dropwise with stirring at 0—10 °C to a mixture of diethyl malonate (9.6 g, 9.2 ml, 0.06 mol) and sodium carbonate (8.4 g) in water (16.0 ml) and ethanol (40.0 ml). The mixture was stirred at room temperature for 1 h and then heated under reflux for 1 h. The insoluble salt was collected from the cooled mixture, combined with a second crop obtained by concentrating the aqueous ethanolic mother liquor, and stirred in dilute aqueous hydrochloric acid overnight to yield the hydrated carboxylic acid (11c), $\nu_{max.}$ 3 600, 3 500, 3 100, 2 700br, and 1 880br (OH, NH), and 1 700br cm^{-1} (CO), which was crystallised from ethanol–glacial acetic acid to give colourless needles of the anhydrous *triazolotriazinonecarboxylic acid* (11c) (8.4 g), m.p. 194° (lit.,[14] 141°), $\nu_{max.}$ 3 100—2 700br (OH), and 1 750, 1 695, and 1 680 cm^{-1} (CO) (Found: C, 33.2; H, 1.8; N, 38.5%; M^+, 181. $C_5H_3N_5O_3$ requires C, 33.1; H, 1.7; N, 38.7%; *M*, 181).

(*b*) The triazolotriazinone ester (11b) (4.2 g, 0.02 mol) was heated under reflux with aqueous M-sodium carbonate (50.0 ml) in ethanol (100 ml) for 1 h. The insoluble salt from the cooled mixture was stirred with dilute aqueous hydrochloric acid for 4 h to give the carboxylic acid (11c) hydrate, crystallisation of which yielded the anhydrous acid (11c) (3.0 g), m.p. 194° (from ethanol–glacial acetic acid), identical (mixed m.p. and i.r. spectrum) with the sample described in (*a*).

[1,2,4]*Triazolo*[5,1-c][1,2,4]*triazin*-7(4H)-*one* (11a).—The anhydrous carboxylic acid (11c) (0.27 g, 0.0015 mol) was heated (oil-bath) in a ' cold finger ' sublimation apparatus at 200—215 °C (14 mmHg). Crystallisation of the colourless sublimate afforded the triazolotriazinone (11a) as colourless prisms (0.16 g), m.p. 236—240° (from ethanol) (lit.,[13] 240°), $\nu_{max.}$ 3 200br and 2 700br (NH) and 1 695 (CO) cm^{-1} (Found: C, 35.1; H, 2.1; N, 51.2%; M^+, 137. Calc. for $C_4H_3N_5O$: C, 35.0; H, 2.2; N, 51.1%; *M*, 137).

Methylation of [1,2,4]*Triazolo*[5,1-c][1,2,4]*triazin*-7(4H)-*one* (11a).—A suspension of the triazolotriazinone (11a) (1.1 g, 0.008 mol) in aqueous 4% w/v sodium hydroxide (12.0 ml) and methanol (12.0 ml) was shaken at room temperature with methyl iodide (2.4 ml) for 17 h. The mixture was concentrated under reduced pressure to remove the methanol and excess of methyl iodide, and extracted with chloroform to give a solid (0.6 g), m.p. 120—136°, which was chromatographed over silica. Elution with chloroform afforded 4-*methyl*[1,2,4]*triazolo*[5,1-c][1,2,4]*triazin*-7-(4H)-*one* (12a) as cream plates (0.34 g), m.p. 174° (sublim.) (from ethanol), $\nu_{max.}$ 1 700br cm^{-1} (CO) (Found: C, 40.0; H, 3.4; N, 46.6%; M^+, 151. $C_5H_5N_5O$ requires C, 39,7; H, 3.3; N, 46.4%; *M*, 151). Further elution with methanol gave the isomeric *N*-methyl derivative (16) or (17) (0.2 g), colourless needles, m.p. 207° (from ethanol–glacial acetic acid), $\nu_{max.}$ 1 690br cm^{-1} (CO) (Found: C, 40.0; H, 3.4; N, 46.9%; M^+, 151. Calc. for $C_5H_5N_5O$: C, 39.7; H, 3.3; N, 46.4%; *M*, 151).

3-*Hydrazino*-2-*methyl*-1,2,4-*triazin*-5(2H)-*one* (18b).—A warm solution of 2-methyl-3-methylthio-1,2,4-triazin-5(2*H*)-one (18a) [15] (0.63 g, 0.004 mol) in propan-2-ol (15.0 ml) was treated with 100% hydrazine monohydrate (1.0 ml) and left at room temperature for 48 h. The precipitated yellow solid was crystallised to yield the pure *hydrazinotriazinone* (18b) as orange plates (0.6 g), m.p. 231° (from dimethylformamide), $\nu_{max.}$ 3 350, 3 200, and 2 700br (NH), and 1 620 cm^{-1} (CO) (Found: C, 34.5; H, 5.0; N, 49.6%; M^+, 141. $C_4H_7N_5O$ requires C, 34.0; H, 5.0; N, 49.6%; *M*, 141).

The hydrazinotriazinone (18b) (0.21 g, 0.0015 mol) was treated with concentrated sulphuric acid (0.6 ml) and then cautiously, with cooling, with methanol (4.5 ml). The mixture was warmed briefly at 100 °C to effect dissolution and then water (1.5 ml) was added, followed by benzaldehyde (0.15 g, 0.0015 mol). The solid which separated was crystallised to afford the *hydrogen sulphate* of the triazine derivative (18c) (0.24 g), cream plates, m.p. 251° (from glacial acetic acid), $\nu_{max.}$ 3 100—2 700br (NH), 1710 (CO), and 1 630br cm^{-1} (C=N) (Found: C, 40.3; H, 3.9; N, 21.3. $C_{11}H_{13}N_5O_5S$ requires C, 40.4; H, 4.0; N, 21.4%), converted by treatment with saturated aqueous sodium hydrogen carbonate into the *benzylidenehydrazinotriazinone* (18c) (quant.), yellow prisms, m.p. 188° (from ethanol), $\nu_{max.}$ 3 200w (NH), 1 685 (CO), and 1 620 cm^{-1} (C=N), τ [$(CD_3)_2$SO] 1.60 (1 H, s, CH), 1.70—2.08 (3 H, m, ArH), 2.48—2.66 (2 H, m, ArH), 2.69 (1 H, s, H-6), and 6.43 (3 H, s, NMe) (Found: C, 57.8; H, 5.0; N, 30.7%; M^+, 229. $C_{11}H_{11}N_5O$ requires C, 57.6; H, 4.8; N, 30.6%; *M*, 229).

4-*Methyl*[1,2,4]*triazolo*[3,4-c][1,2,4]*triazin*-7(4H)-*one* (13d).—The hydrazinotriazinone (18b) (0.21 g, 0.0015 mol) was heated under reflux in 98—100% formic acid (4.0 ml) for 10 min. The mixture was evaporated and treated with water to afford the N-*methyltriazolotriazinone* (13c) (0.14 g) as colourless plates, m.p. 166° (from ethanol), $\nu_{max.}$ 1 700 cm^{-1} (CO) (Found: C, 39.5; H, 3.3; N, 46.2%; M^+, 151. $C_5H_5N_5O$ requires C, 39.7; H, 3.3; N, 46.4%; *M*, 151).

4-*Methyl*[1,2,4]*triazolo*[5,1-c][1,2,4]*triazin*-7(4H)-*one* (12a).—(*a*) The hydrazinotriazinone (18b) or the *N*-methyltriazolotriazinone (13d) (0.0015 mol) was heated under reflux in 98—100% formic acid (4.0 ml) for 51 h. Alternatively (*b*) the *N*-methyltriazolotriazinone (13d) (0.1 g, 0.0007 mol) was heated under reflux with anhydrous sodium acetate (0.06 g) in water (1.0 ml) and ethanol (2.0 ml) for 1.5 h. The mixtures were evaporated and treated with water to yield the *N*-methyltriazolotriazinone (12a) (60—90%), m.p. 174° (sublim.) (from ethanol), identical (mixed m.p. and i.r. spectrum) with a sample prepared before.

Ethyl 7-*Methyl*[1,2,4]*triazolo*[5,1-c][1,2,4]*triazine*-6-*carboxylate* (21c).—A solution of 1,2,4-triazole-5-diazonium nitrate (0.03 mol) in dilute aqueous nitric acid (prepared as described before) was added dropwise at 0—10 °C to a stirred solution of ethyl acetoacetate (3.9 g, 3.8 ml, 0.03 mol) and anhydrous sodium acetate (3.2 g) in water (8.0 ml) and ethanol (20.0 ml). After stirring at room temperature for 2 h, the mixture (containing a solid) was concentrated, and treated with water and dilute aqueous hydrochloric acid. Crystallisation of the resulting solid gave the hemihydrate of the *triazolotriazine* (21c), as cream prisms (2.7 g), m.p. 189° (from ethanol–glacial acetic acid), $\nu_{max.}$ 3 300 and 3 200—2 700br (OH) and 1 720br cm^{-1} (CO) (Found: C, 44.7; H, 4.4; N, 32.2. $C_8H_9N_5O_2$,0.5H_2O requires C, 44.4; H, 4.6; N, 32.4%), M^+ 207.

7-Methyl[1,2,4]*triazolo*[5,1-c][1,2,4]*triazine-6-carboxylic Acid* (21d).—The hemihydrate of the ester (21c) (0.86 g, 0.004 mol) was heated under reflux with aqueous M-sodium carbonate (10.0 ml) in ethanol (20.0 ml) for 2 h. The mixture was concentrated and treated with dilute aqueous sulphuric acid to afford starting material (0.28 g), m.p. 189° (from ethanol–glacial acetic acid). Continuous extraction with chloroform of the aqueous mother liquor gave the *carboxylic acid* (21d) as a cream solid (0.19 g), m.p. 165° (decomp.) (from ethyl acetate–light petroleum), $\nu_{max.}$ 3 150 and 2 700br (OH) and 1 720br cm^{-1} (CO) (Found: C, 40.2; H, 3.0; N, 38.5%; M^+, 179. $C_6H_5N_5O_2$ requires C, 40.2; H, 2.8; N, 39.1%; *M*, 179).

7-Amino[1,2,4]*triazolo*[5,1-c][1,2,4]*triazine-6-carboxamide* (23b).—A solution of 1,2,4-triazole-5-diazonium nitrate (0.03 mol) in dilute aqueous nitric acid (prepared as described before) was added dropwise at 0—10 °C to a stirred solution of cyanoacetamide (2.52 g, 0.03 mol) and anhydrous sodium acetate (3.2 g) in water (8.0 ml) and ethanol (20.0 ml). The mixture (containing a solid) was stirred at room temperature for 2 h and was then concentrated. The resulting solid (3.7 g) was boiled with water leaving resinous material (1.9 g) insoluble. Evaporating the aqueous extract gave the amino-amide (23b), more of which was recovered by evaporating the aqueous ethanolic mother liquor and treating with water. Crystallisation from water gave the hemihydrate of the *amino-amide* (23b) (1.3 g), m.p. >220° (decomp.), $\nu_{max.}$ 3 400, 3 250, and 3 100—2 700br (NH, OH), 1 680 (CO), and 1 650 cm^{-1} (NH def.) (Found: C, 32.1; H, 3.0; 52.3. $C_5H_5N_7O,0.5H_2O$ requires C, 31.9; H, 3.2; N, 52.1%), M^+ 179.

Acid-catalysed Hydrolysis of the Amino[1,2,4]*triazolo*[5,1-c]-[1,2,4]*triazines* (23a *and* b).—The amines (23a and b) (0.004 mol) were heated under reflux with aqueous 2M-sulphuric acid (7.5 ml) in ethanol (20.0 ml) for 3 h. The solid which separated from the concentrated mixture was combined with material obtained by extracting the aqueous mother liquor with chloroform, and crystallised to yield the triazolotriazinones (11d) (53%), m.p. >310° (from dimethylformamide) and (11e) (73%), m.p. 255° (from glacial acetic acid), identical (mixed m.p. and i.r. spectrum) with authentic samples.

4,7-Dihydro-7-oxo[1,2,4]*triazolo*[5,1-c][1,2,4]*triazine-6-carboxamide* (11d).—A solution of the ester (11b) (0.64 g, 0.003 mol) in absolute ethanol (100 ml) was saturated at 0 °C with dry ammonia gas, stoppered, and left at room temperature for 24 h. The mixture was evaporated, treated with water, acidified (dilute aqueous sulphuric acid), and extracted with chloroform. The solid obtained from the extract was heated under reflux with ethanol to remove the ester (11b), leaving the insoluble *amide* (11d) (0.08 g), m.p. >310° (from dimethylformamide), $\nu_{max.}$ 3 350, 3 200, and 2 700br (NH), 1 740 and 1 670 (CO), and 1 640 cm^{-1} (NH def.) (Found: C, 34.0; H, 2.5; N, 46.2%; M^+, 180. $C_5H_4N_6O_2$ requires C, 33.3; H, 2.2; N, 46.7%; *M*, 180).

6-Benzoyl-4-methyl[1,2,4]*triazolo*[5,1-c][1,2,4]*triazin-7(4H)-one* (12c).—The ketone (11e) (0.36 g, 0.0015 mol) in anhydrous acetone (50.0 ml) was heated under reflux with dimethyl sulphate (0.9 ml) and anhydrous potassium carbonate (1.6 g) for 4 h. The filtered mixture was evaporated, treated with water, and extracted with chloroform to give an oil, which was triturated with ether–methanol to afford the *N-methyltriazolotriazinone* (12c) (0.23 g), colourless prisms, m.p. 166° (from ethanol), $\nu_{max.}$ 1 730br and 1 660 cm^{-1} (CO) (Found: C, 56.7; H, 3.7; N, 27.3%; M^+, 255. $C_{12}H_9N_5O_2$ requires C, 56.5; H, 3.5; N, 27.4%; *M*, 255).

Attempted Diazotisation of 7-Amino-6-benzoyl[1,2,4]*triazolo*[5,1-c][1,2,4]*triazine* (23a).—(*a*) A stirred solution of the amino-ketone (23a) (0.72 g) in glacial acetic acid (10.0 ml) containing aqueous 90% w/v sulphuric acid (5.0 ml) was treated dropwise at <5 °C with a solution of sodium nitrite (0.35 g) in water (10.0 ml). The mixture was stirred at <5 °C for 15 min, then diluted with water to afford the starting amine (23a) (0.61 g), m.p. 224° (from benzene–glacial acetic acid).

(*b*) A stirred solution of the amino-ketone (23a) (0.24 g, 0.001 mol) in 1,2-dimethoxyethane (3.0 ml) was treated dropwise at 0 °C with pentyl nitrite (0.12 g, 0.14 ml, 0.001 mol). After stirring at 0 °C for 45 min the mixture was treated with glacial acetic acid (3.0 ml) and stirred at room temperature for 17 h. The precipitated solid was combined with a second crop obtained by evaporating the mother liquor and triturating with benzene to afford the unchanged amino-ketone (23a) (0.17 g).

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