141. *The Preparation of Fused Triazole Systems.*

By J. D. Bower and F. P. Doyle.

Derivatives of 3 : 4-fused 1 : 2 : 4-triazoles and 1 : 5-fused tetrazoles have been obtained from nitrogen-heterocycles bearing a 2-hydrazino-group. The reactions of ethyl acetoacetate and acetylacetone with 3-amino-1 : 2 : 4-triazole lead to ring formation involving the amino-group and the 4-nitrogen atom of the triazole ring, but reaction of acetylacetone with 3-amino-5-phenyl-1 : 2 : 4-triazole involves the 2-nitrogen atom.

The preparation of fused triazole and tetrazole systems by the formation of a five-membered ring between a heterocyclic nitrogen atom and a 2-hydrazino-group appears to have been first reported by Marckwald and Meyer.[1] These workers prepared *s*-triazolo-[4,3-*a*]quinoline (I) by the action of formic acid on 2-quinolylhydrazine; later Marckwald and Rudzik,[2] Fargher and Furness,[3] and Graf and his co-workers [4] prepared similar compounds from 2-pyridylhydrazines. More recently Druey and Ringier [5] reported related work on hydrazinophthalazines and extended the formic acid condensation to the use of other acids and acid chlorides.

[1] Marckwald and Meyer, *Ber.*, 1900, **33**, 1885.
[2] Marckwald and Rudzik, *Ber.*, 1903, **36**, 1111.
[3] Fargher and Furness, *J.*, 1915, 688.
[4] Graf, Lederer-Ponzer, Kopetz, Purkert, and Laszlo, *J. prakt. Chem.*, 1933, **138**, 244.
[5] Druey and Ringier, *Helv. Chim. Acta*, 1951, **34**, 195.

As part of another investigation some of the above reactions have been extended to other heterocyclic hydrazines. The action of benzoyl chloride in pyridine on 2-pyridylhydrazine gave the benzoyl derivative (II) and, in contrast to the experiences of Druey and Ringier [5] in similar reactions, it was found necessary to heat this with phosphoryl chloride to effect ring closure to 3-phenyl-*s*-triazolo[4,3-*a*]pyridine (III). This compound was also obtained by dehydrogenation of benzaldehyde 2-pyridylhydrazone (IV) with lead tetra-acetate, a reagent used in an analogous synthesis of benziminazoles from Schiff's bases of

TABLE 1. *Hydrazones.*

No.	Hydrazone	Cryst.[a] from	M. p.	Formula	Found (%) C	H	N	Required (%) C	H	N
1	p-*Bromobenzaldehyde* 4-*hydroxy*-6-*methyl*-2-*pyrimidyl*-	G[b]	272°	$C_{12}H_{11}ON_4Br$	—	—	18·3[*]	—	—	18·2[*]
2	m-*Nitrobenzaldehyde* 4-*hydroxy*-6-*methyl*-2-*pyrimidyl*-	A[c]	285 (decomp.)	$C_{12}H_{11}O_3N_5$	53·4	4·5	26·0	52·7	4·1	25·6
3	*Benzaldehyde* 4 : 6-*dimethyl*-2-*pyrimidyl*-[d]	H	161	$C_{13}H_{14}N_4$	68·9	6·2	—	69·0	6·2	—
4	p-*Bromobenzaldehyde* 4 : 6-*dimethyl*-2-*pyrimidyl*-[e]	B	164	$C_{13}H_{13}N_4Br$	51·1	4·0	—	51·2	4·3	—
5	*Benzaldehyde* 6-*methyl*-4-*pyrimidyl*-[e]	E	209	$C_{12}H_{12}N_4$	68·3	5·7	—	67·9	5·7	—
6	*Benzaldehyde* 5-*nitro*-2-*pyridyl*-	F[f]	233	$C_{12}H_{10}O_2N_4$	59·3	4·2	—	59·5	4·2	—
7	p-*Bromobenzaldehyde* 2-*benzothiazolyl*-	F[e]	280	$C_{14}H_{10}N_3SBr$	50·4	3·1	12·6	50·6	3·0	12·6

[*] Needles (except as stated), from: A, acetic acid; B, benzene; C, 2-methoxyethanol; D, water; E, aqueous ethanol; F, industrial methylated spirit; G, ethyl methyl ketone; H, ligroin; J, ethyl acetate. [b] Prisms. [c] Pale yellow. [d] Prepared from 4 : 6-dimethyl-2-pyrimidylhydrazine [13] in benzene by azeotropic removal of water. [e] Prepared in ethanol. [f] Brown.

[*] Found: Br, 25·9; Reqd.: Br, 26·0%.

TABLE 2. *Aryltriazoles.*[*]

Compound	From hydrazone no.	Cryst.[a] from	M. p.	Formula	Found (%) C	H	N	Required (%) C	H	N
5-*Hydroxy*-7-*methyl*-3-*phenyl*-s-*triazolo*-[4,3-a]*pyrimidine*[b]	—	A, then F	<340°	$C_{12}H_{10}ON_4$	63·7	4·3	—	63·7	4·5	—
3-p-*Bromophenyl*-5-*hydroxy*-7-*methyl*-s-*triazolo*[4,3-a]*pyrimidine*	1	A	<340	$C_{12}H_9ON_4Br$	47·2	3·0	—	47·2	3·0	—
5-*Hydroxy*-7-*methyl*-3-m-*nitrophenyl*-s-*triazolo*[4,3-a]*pyrimidine*	2	A	<340	$C_{12}H_9O_3N_5,H_2O$	50·3	3·6	24·1	49·8	3·8	24·2
5 : 7-*Dimethyl*-3-*phenyl*-s-*triazolo*-[4,3-a]*pyrimidine*	3	B[c]	260	$C_{13}H_{12}N_4$	—	—	25·2	—	—	25·0
7-*Methyl*-3-*phenyl*-s-*triazolo*[4,3-c]*pyrimidine*	5	H	187	$C_{12}H_{10}N_4,CH_2{\cdot}CO_2H$	62·2	5·2	20·8	62·2	5·2	20·7
5-*Nitro*-3-*phenyl*-s-*triazolo*[4,3-a]*pyridine*	6	J[d]	207	$C_{12}H_8O_2N_4$	60·6	3·6	—	60·0	3·4	—
3-*Phenyl*-s-*triazolo*-[3,4-b]*benzothiazole*[e]	—	B	229	$C_{14}H_9N_3S,CH_3CO_2H$	62·0	4·2	13·5	61·7	4·2	13·5
3-p-*Bromophenyl*-s-*triazolo*[3,4-b]-*benzothiazole*[f]	7	B	240	$C_{14}H_8N_3BrS,CH_3{\cdot}CO_2H$	—	—	10·5	—	—	10·8
Diphenyl-s-*triazolo*-s-*triazole*[g]	—	C	268	$C_{15}H_{11}N_5$	69·0	4·3	—	68·9	4·2	—

[*] Prepared in acetic acid, except for the fourth compound, which was prepared in benzene.

[a] See footnote *a* of Table 1. [b] Prepared from benzaldehyde 4-hydroxy-6-methyl-2-pyrimidylhydrazone.[8,15] [c] Plates. [d] Yellow. [e] Prepared from benzaldehyde 2-benzothiazolylhydrazone, m. p. 228°.[12,16] [f] Found: Br, 21·3. Reqd.: Br, 20·5%. [g] Structure uncertain; prepared from benzaldehyde 5-phenyl-1 : 2 : 4-triazolyl-3-hydrazone.[17]

o-diamines.[6] This method of ring closure has been successfully applied to other arylhydrazones (Table 1) to give the triazoles shown in Table 2.

Tarbell *et al.*[7] reported the reaction of 2-pyridylhydrazine with one equivalent of carbon disulphide to give 3-mercapto-*s*-triazolo[4,3-*a*]pyridine (V). We have applied a similar treatment to other hydrazines to prepare the fused mercaptotriazoles shown in Table 3.

By the methods of ring formation described above, 2-pyrimidylhydrazines which are not symmetrically substituted at positions 4 and 6 (*e.g.*, VI; R = OH) might each give one or both of two isomeric products. When 4-hydroxy-6-methyl-2-pyrimidylhydrazine (VI; R = OH) was treated with benzoyl chloride followed by phosphoryl chloride, formation of the triazole ring was accompanied by replacement of the hydroxyl group by chlorine to give a product which may be formulated as (VII or VIII; R = Cl). Cyclisation of the hydrazone (IX) with lead tetra-acetate gave a compound which, likewise, may

TABLE 3. *Mercaptotriazoles.*

Compound	Cryst.[a] from	M. p.[a]	Formula	Found (%)	Required (%)
3-*Mercapto*-9H-s-*triazolo*[3,4-b]*benziminazole*[b]	E	284°	$C_8H_6N_4S$	N, 29·3; S, 16·7	N, 29·5; S, 16·9
3-*Mercapto*-s-*triazolo*[3,4-b]*benzothiazole*	B	255	$C_8H_5N_3S_2$	C, 46·6; H, 2·6	C, 46·4; H, 2·4
5 : 7-*Dimethyl*-3-*mercapto*-s-*triazolo*[4,3-a]*pyrimidine*[c]	D[c]	241	$C_7H_8N_4S$	C, 46·8; H, 4·6	C, 46·6; H, 4·5
5-*Hydroxy*-3-*mercapto*-7-*methyl*-s-*triazolo*[4,3-a]*pyrimidine*[d]	D	273	$C_6H_6ON_4S$	N, 30·9	N, 30·8

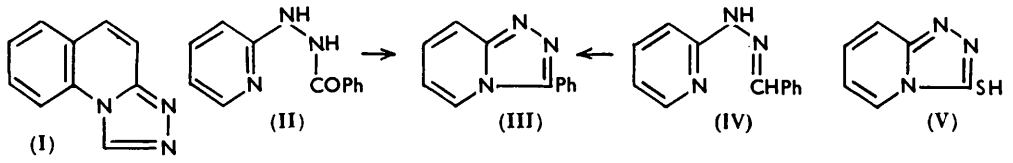
[a] See footnote *a* of Table 1. [b] From 2-benziminazolylhydrazine, prepared from the sulphonic acid [18] by reaction with hydrazine hydrate (90%) for 10 min. under reflux.[18] [c] Lemon-yellow product; reaction with chloroacetic acid in water gave 3-*carboxymethylthio*-5 : 7-*dimethyl*-s-*triazolo*[4,3-a]*pyrimidine* as needles, m. p. 183°, from water (Found: C, 45·4; H, 4·2. $C_9H_{10}O_2N_4S$ requires C, 45·4; H, 4·2%). [d] Cream prisms; reaction with chloroacetic acid in water gave 3-*carboxymethylthio*-5-*hydroxy*-7-*methyl*-s-*triazolo*[4,3-a]*pyrimidine* as needles, m. p. 251° (decomp.), from water (Found: C, 40·2; H, 3·6; S, 13·7. $C_8H_8O_3N_4S$ requires C, 40·0; H, 3·4; S, 13·3%). [e] With decomp.

have either structure (VII; R = OH) or (VIII; R = OH) and was converted by phosphoryl chloride into the same chloro-compound as was obtained from the phosphoryl chloride cyclisation mentioned above. Evidence concerning the structure of these compounds was provided by the work of Birr [8a] and Birr and Walther [8b] published while the present work was in progress. They showed that the reaction of formic acid with 4-hydroxy-6-methyl-2-pyrimidylhydrazine (VI; R = OH) (reaction *a*) gave the same compound as that previously said to be (XIII; R = OH, R′ = Me, R″ = H) prepared by Bulow and Haas [9] by the action of ethyl acetoacetate on 3-amino-1 : 2 : 4-triazole (X; R = H) (reaction *b*). They also produced evidence suggesting that in the latter reaction the amino-group of (X; R = H) reacts preferentially with the keto- rather than with the ester group of ethyl acetoacetate and thus that the product of reactions *a* and *b* has the structure (XI). It therefore appears that cyclisations of derivatives of our hydrazine (VI; R = OH) involve the nitrogen atom adjacent to the hydroxyl group, and the products obtained in the present work have been formulated accordingly.

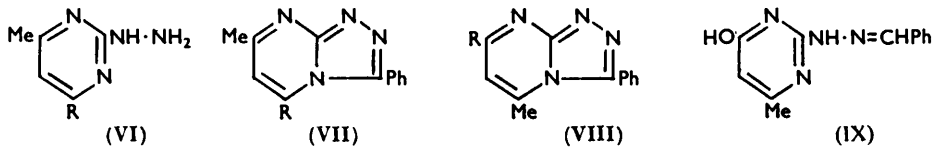
The conclusions reached by Birr and Walther [8] as to the reactive nitrogen of the triazole ring of (X; R = H) have been confirmed by a study of the simpler case of 4 : 6-dimethyl-2-pyrimidylhydrazine (VI; R = Me). This compound with formic acid gave the same product (XII) as did the reaction between acetylacetone and 3-amino-1 : 2 : 4-triazole (X; R = H). The latter reaction, therefore, like that of (X; R = H) with ethyl acetoacetate, involved the 4-nitrogen atom of the triazole ring rather than, as assumed by Bulow and Haas,[9] the 2-nitrogen atom.

[6] Stephens, *Nature*, 1949, **164**, 342; Stephens and Bower, *J.*, 1949, 2971; 1950, 1772.
[7] Tarbell, Todd, Paulson, Lindstrom, and Wystrack, *J. Amer. Chem. Soc.*, 1948, **70**, 1381.
[8] (*a*) Birr, *Z. wiss. Photogr. Photophysik. Photochem.*, 1952, **47**, 8; (*b*) Birr and Walther, *Chem. Ber.*, 1953, **86**, 1401.
[9] Bulow and Haas, *Ber.*, 1909, **42**, 4638.

In contrast, however, cyclisation of benzaldehyde 4 : 6-dimethyl-2-pyrimidylhydrazone gave the triazolopyrimidine (VII; R = Me) which was different from the product from the reaction of 3-amino-5-phenyl-1 : 2 : 4-triazole (X; R = Ph) with acetylacetone. This

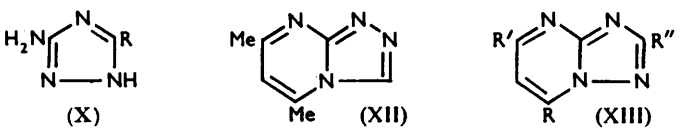


(I) (II) (III) (IV) (V)

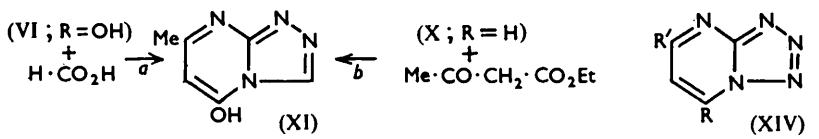


(VI) (VII) (VIII) (IX)

is therefore formulated as the isomeric structure (XIII; R = R′ = Me, R″ = Ph), cyclisation having involved the 2-nitrogen atom of the triazole (X; R = Ph). The triazolopyrimidine obtained from the reaction of the triazole (X; R = Ph) with ethyl acetoacetate was also found to be different from that obtained by the cyclisation of benzaldehyde



(X) (XII) (XIII)



(XI) (XIV)

4-hydroxy-6-methyl-2-pyrimidylhydrazine and assigned by us the structure (VII; R = OH). Since no direct evidence exists as to whether the keto- or ester grouping of ethyl acetoacetate will react primarily with the amino-group of 3-amino-5-phenyl-1 : 2 : 4-triazole it is not possible to assign a definite structure to the product from this reaction, the alternatives (VIII; R = OH), (XIII; R = Me, R′ = OH, R″ = Ph) and (XIII; R = OH, R′ = Me, R″ = Ph) being feasible, the last being preferred on the basis of the present work and by analogy with the evidence of Birr [8a] and Birr and Walther.[8b]

The known reaction of heterocyclic hydrazines with nitrous acid to form fused tetrazoles has been applied to some of the hydrazines prepared during the present work. It is noteworthy that such a reaction, using 4-hydroxy-6-methyl-2-pyrimidylhydrazine (VI; R = OH), gave a compound apparently identical with that obtained by Bulow [10] from the reaction of 5-aminotetrazole with ethyl acetoacetate. Of the two probable formulæ, (XIV; R = OH, R′ = Me and *vice versa*), for this compound the analogy of the triazoles suggests the former, which is also that assumed by Bulow.

Experimental

M. p.s are corrected.

6-Methyl-4-pyrimidylhydrazine.—6-Methyl-4-methylthiopyrimidine [11] (3·4 g.) was heated under reflux with 90% hydrazine hydrate (5 c.c.) for 1 hr. The solid (2·1 g.) was removed from

[10] Bulow, *Ber.*, 1909, **42**, 4429.
[11] Marshall and Walker, *J.*, 1951, 1004.

the cooled mixture and crystallised from benzene, to give the *hydrazine* as needles, m. p. 140° (Found : C, 48·7; H, 6·2. $C_5H_8N_4$ requires C, 48·4; H, 6·5%).

4-Hydroxy-6-methyl-2-pyrimidylhydrazine (VI; R = OH).[8b]—This hydrazine, m. p. 240°, was prepared from 6-methyl-2-thiouracil and alcoholic hydrazine hydrate in 55% yield (Found : N, 39·6. Calc. for $C_5H_8ON_4$: N, 40·0%).

Hydrazones.—Details of hydrazones not previously described are given in Table 1. Except where otherwise stated they were prepared in 50% aqueous acetic acid.

Aryl-substituted Fused Triazoles.—These were prepared in acetic acid or benzene solution by the action of lead tetra-acetate on the appropriate hydrazone, and are listed in Table 2. The yields of crude material exceeded 50%. The following examples illustrate the experimental methods.

*3-Phenyl-*s*-triazolo*[4,3-a]*pyridine* (III). (*a*) Lead tetra-acetate (2·2 g.) was added to a benzene solution of benzaldehyde 2-pyridylhydrazone [3] (1·0 g.). The mixture was warmed to complete the reaction, water was added, and the benzene was removed by steam-distillation. The crystals (0·6 g.), m. p. 175°, which formed in the cooled residue, were recrystallised from benzene and gave the *triazolopyridine* as plates, m. p. 176° (Found : C, 73·9; H, 4·4; N, 21·6. $C_{12}H_9N_3$ requires C, 73·8; H, 4·6; N, 21·5%). The *picrate*, from methanol, formed yellow needles, m. p. 234° (Found : C, 50·7; H, 2·9. $C_{12}H_9N_3,C_6H_3O_7N_3$ requires C, 50·9; H, 2·9%).

(*b*) Benzoyl chloride (7·0 c.c.) was slowly added to an ice-cold solution of 2-pyridylhydrazine (5·5 g.) in pyridine (50 c.c.). After 30 min. the solution was heated for 1 hr. on the water-bath and poured into cold water (*ca.* 200 c.c.). The crude *N-benzoyl-N'-2-pyridylhydrazine* (7·9 g.), m. p. 184—188°, was crystallised from 50% aqueous propylene glycol for use in the next stage. A sample, crystallised twice from xylene, formed needles, m. p. 193° (Found : C, 67·9; H, 5·1. $C_{12}H_{11}ON_3$ requires C, 67·6; H, 5·2%). The once crystallised benzoyl compound (3·9 g.) was heated under reflux for 3 hr. with phosphoryl chloride (13 c.c.). The excess of phosphoryl chloride was removed under reduced pressure and the residue was decomposed with ice and sodium hydroxide solution. The solid product (2·3 g.) was removed and crystallised from benzene as plates, m. p. 176°. Both the base and its picrate, m. p. 234°, were identical (mixed m. p.s) with those prepared by method (*a*).

*3-p-Bromophenyl-5 : 7-dimethyl-*s*-triazolo*[4,3-a]*pyrimidine.* *p*-Bromobenzaldehyde 4 : 6-dimethyl-2-pyrimidylhydrazone (1·0 g.) and lead tetra-acetate (1·5 g.) were allowed to react in acetic acid (5 c.c.). On the addition of water a precipitate (0·7 g.) was formed which crystallised from ethanol. The *triazolopyrimidine* formed plates, m. p. 286° (decomp.) (Found : C, 51·3; H, 3·7. $C_{13}H_{11}N_4Br$ requires C, 51·5; H, 3·7%).

Mercapto-substituted Fused Triazoles.—The thiols detailed in Table 3 were prepared from the hydrazine in hot aqueous ethanol in the presence of one equivalent of potassium hydroxide and an excess of carbon disulphide until the evolution of hydrogen sulphide was complete. The thiol was liberated by dilute acid.

5-Hydroxy-7-methyltetrazolo[1,5-a]*pyrimidine* (XIV; R = OH, R' = Me).—A solution of sodium nitrite (1·5 g.) in water (5 c.c.) was added to a solution of 4-hydroxy-6-methyl-2-pyrimidylhydrazine (2·8 g.) in N-hydrochloric acid solution (20 c.c.), and the suspension was heated to the b. p. The precipitate (2·6 g.) which was formed from the cooled solution crystallised from aqueous alcohol and then water as needles, m. p. 253° (previous decomp.) (Found : C, 39·6; H, 3·2. Calc. for $C_5H_5ON_5$: C, 39·7; H, 3·3%). Light absorption in 0·082N-NaOH : Max. at 219 mμ (log ε 4·33) and 276 mμ (log ε 3·47); min. at 259 mμ (log ε 3·37). The m. p. was undepressed on admixture of the compound, m. p. 253° (decomp.), prepared from ethyl acetoacetate and 5-aminotetrazole, for which Bulow [10] reported m. p. 246—247°. Light absorption in 0·082N-NaOH as above.

The following *tetrazoles* were prepared similarly : *Tetrazolo*[5,1-b]*benzothiazole* (from 2-benzothiazolylhydrazine), colourless needles, m. p. 109°, from water (Found : C, 47·2; H, 2·2. Calc. for $C_7H_4N_4S$: C, 47·7; H, 2·3%), stable to light. Colonna and Andrisano [12] obtained this tetrazole as orange needles, becoming red in the light, m. p. 111°.

9H-*Tetrazolo*[5,1-b]*benziminazole* (from 2-benziminazolylhydrazine; see note *b*, Table 3), needles, m. p. 189° (decomp.), from aqueous methanol, becoming dark in light (Found : C, 52·5; H, 3·4. $C_7H_5N_5$ requires C, 52·8; H, 3·2%).

[12] Colonna and Andrisano, *Pubblicazioni dell'istituto di chimica industriale dell università di Bologna*, 1943, No. 5, 3; through *Chem. Abs.*, 1947, **41**, 754.

5-Chloro-7-methyl-3-phenyl-s-triazolo[4,3-a]*pyrimidine* (VII; R = Cl).—(*a*) 5-Hydroxy-7-methyl-3-phenyl-*s*-triazolo[4,3-*a*]pyrimidine (2·2 g.) was heated under reflux in phosphoryl chloride (10 c.c.) and dimethylaniline (2·2 c.c.) for 2 hr. The excess of solvent was removed under vacuum and the complex was decomposed with ice and basified, yielding a brown solid. This formed needles (0·55 g.) of the *triazolopyrimidine*, m. p. 218°, on crystallisation from 2-methoxyethanol (Found: C, 58·7; H, 3·8. $C_{12}H_9N_4Cl$ requires C, 58·9; H, 3·7%).

(*b*) Benzoyl chloride (4·0 c.c.) was slowly added to an ice-cold suspension of 4-hydroxy-6-methyl-2-pyrimidylhydrazine (4·2 g.) in pyridine (20 c.c.). The mixture was heated on a steam-bath for 30 min., and poured into water, *N-benzoyl-N'-4-hydroxy-6-methyl-2-pyrimidylhydrazine* (6·2 g.) separating. This was crystallised twice from ethylene glycol, as needles, m. p. 286° (Found: C, 58·4; H, 5·1; N, 23·0. $C_{12}H_{12}O_2N_4$ requires C, 59·0; H, 4·9; N, 22·9%). This benzoyl compound (2·6 g.) was heated under reflux with phosphoryl chloride (12 c.c.) for 30 min. and the crude product (1·2 g.) was isolated in the usual manner. On crystallisation from 2-methoxyethanol it formed small needles, m. p. 218°, not depressed on admixture with those obtained by method (*a*).

5 : 7-*Dimethyl-s-triazolo*[4,3-a]*pyrimidine* (XII).—4 : 6-Dimethyl-2-pyrimidylhydrazine [13] (1·0 g.) was boiled under reflux for 4 hr. with 98% formic acid (3 c.c.). The excess of acid was removed under reduced pressure on the water-bath and the residue was crystallised first from benzene–ligroin and then from ethyl acetate as long needles, m. p. 136° (Found: C, 56·2; H, 5·5. Calc. for $C_7H_8N_4$: C, 56·7; H, 5·4%). The m. p. was undepressed on admixture of the compound, m. p. 136°, prepared from acetylacetone and 3-amino-1 : 2 : 4-triazole (Bulow and Haas [9] reported m. p. 133°).

5 : 7-*Dimethyl-2-phenyl-s-triazolo*[2,3-a]*pyrimidine* (XIII; R = R' = Me, R'' = Ph).—A solution of 3-amino-5-phenyl-1 : 2 : 4-triazole [14] (1·6 g.) and acetylacetone (1·1 g.) in acetic acid (7·5 c.c.) was heated under reflux for 1½ hr. and then evaporated to dryness under reduced pressure on the water-bath. Dilute aqueous sodium hydroxide and chloroform were added, the mixture was shaken well, and the chloroform layer removed. The aqueous layer was extracted again with chloroform and the combined chloroform extracts were evaporated to dryness. Crystallisation of the residue from methanol gave the *triazolopyrimidine* (2·0 g.) as needles, m. p. 174°. Recrystallisation raised the m. p. to 175° (Found: C, 70·0; H, 5·7. $C_{13}H_{12}N_4$ requires C, 69·6; H, 5·4%). When the reaction was carried out (2 hr.) in boiling ethanol containing a drop of piperidine, a compound (1·4 g.) was obtained which was presumably *acetylacetone bis-5-phenyl-1 : 2 : 4-triazol-3-ylimine*. It formed needles, m. p. 230°, from methanol (Found: C, 65·6; H, 5·3; N, 29·3. $C_{21}H_{20}N_8$ requires C, 65·6; H, 5·2; N, 29·2%).

Triazolopyrimidine from 3-Amino-5-phenyl-1 : 2 : 4-triazole and Ethyl Acetoacetate.—3-Amino-5-phenyl-1 : 2 : 4-triazole (2·2 g.) and ethyl acetoacetate (1·8 g.) were heated under reflux for 3 hr. in acetic acid (10 c.c.). The cooled solution deposited the crystalline *triazolopyrimidine* (2·5 g.). Recrystallisation from 2-ethoxyethanol gave prisms, m. p. >340° (Found: C, 63·2; H, 4·6. $C_{12}H_{10}ON_4$ requires C, 63·7; H, 4·5%).

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British Photographic Industries Ltd.,
Fulbourne Road, Walthamstow, E.17.

[Present addresses:
J. D. B., 39A, Louis Street, Spring Bank,
Hull, Yorks.
F. P. D., Beecham Research Labs. Ltd.,
Brockham Park, Betchworth, Surrey.]

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[14] Hoggarth, *J.*, 1950, 612.
[15] Thiele and Bihan, *Annalen*, 1898, **302**, 299.
[16] Ebros and Davidenkov, *J. Gen. Chem., U.S.S.R.*, 1951, **21**, 2046.
[17] Manchot, *Ber.*, 1910, **43**, 1312.
[18] Everett, *J.*, 1930, 2402.
[19] Cf. G.P. 614,327.