Thermal Cyclisation of Pyridazinylhydrazones to give *s*-Triazolo[4,3-*b*]-pyridazines and Pyridazino[2,3-*a*]benzimidazole

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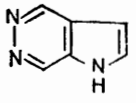
Thermal (non-catalytic) cyclisation of 6-methylpyridazin-3-ylhydrazones (14) unexpectedly caused ring closure on to the 2-nitrogen atom of the ring, usually without elimination of ammonia but with elimination of the elements of a hydrocarbon, to give 3-substituted 6-methyl-*s*-triazolo[4,3-*b*]pyridazines [*e.g.* (21)]. Cyclohexanone 6-methylpyridazin-3-ylhydrazone (38) gave both 6-methyl-3-pentyl-*s*-triazolo[4,3-*b*]pyridazine (42) and 6,7,8,9-tetrahydro-2-methylpyridazino[2,3-*a*]benzimidazole (43).

HETEROCYCLIC nuclei which can be considered as mono- or di-aza-derivatives of indole have potential pharmacological interest because of their close relationship with



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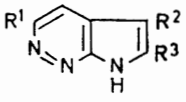
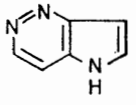


(3) $R^1=R^2=R^3=H$
(4) $R^1=Me, R^2=H, R^3=CH_2\cdot CH_2\cdot CN$
(5) $R^1=Me, R^2=H, R^3=CH_2\cdot CH_2\cdot CO_2Et$
(6) $R^1=Me, R^2=Br, R^3=CH_2\cdot CH_2\cdot CO_2Et$
(13) $R^1=H$, R^2 and $R^3 \neq H$
(15) $R^1=Me$, R^2 and $R^3 \neq H$
(19) $R^1=R^2=Me, R^3=Et$
(20) $R^1=Me, R^2=Ph, R^3=CH_2Ph$



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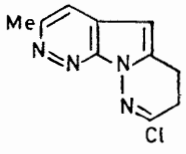

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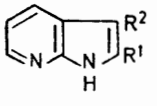
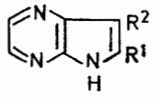


(8) R^1 and $R^2 \neq H$

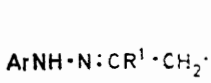


(9) R^1 and $R^2 \neq H$

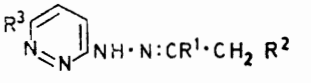
indoles and purines. Representatives of all the three possible pyrrolopyridazines (1)—(3) are known.[1] However, the first route to (2) was reported [1] only recently, and only three examples [(4)—(6)] of the 7*H*-pyrrolo-[2,3-*c*]pyridazine system (3) have been described.[2] The cyanide (4) was obtained as a by-product when 8-chloro-6,7-dihydro-3-methyldipyridazino[2,3-*a*:4,3-*d*]pyrrole (7) was treated with hydrogen and ammonia in the presence of palladised charcoal, presumably by cleavage of the N–N bond and elimination of hydrogen chloride. Compounds (5) and (6) were obtained as derivatives of (4).

Our success in obtaining pyrrolopyridines [3,4] [*e.g.* (8)] and pyrrolopyrazines [5] (9) by thermal (non-catalytic) cyclisation of the appropriate hydrazones (10) and (11) respectively, encouraged us to think that a similar reaction might occur with pyridazin-3-ylhydrazones (12) to give substituted pyrrolo[2,3-*c*]pyridazines (13). We chose to prepare and study the cyclisation of 6-methylpyridazin-3-ylhydrazones (14) because (i) the corresponding hydrazine is accessible by a known route; (ii) the methyl substituent is unlikely to cause unwanted reactions which might be encountered if the more readily accessible 6-chloro-3-hydrazinopyridazine were employed; (iii) cyclisation of (14) to a suitably substituted pyrrolopyridazine (15) might afford a route to a known example (4) of the ring system.

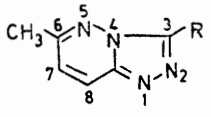
3-Hydrazino-6-methylpyridazine was readily converted into a series of crystalline hydrazones by reactions with ketones and an aldehyde (Table 1). The ^1H n.m.r. spectra (Table 2) of the hydrazones all showed a signal at



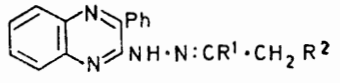
(10) Ar = 2-pyridyl
(11) Ar = pyrazin-2-yl
(12) Ar = pyridazin-3-yl
(23) Ar = 4-pyrimidyl



(14) R^1 and $R^2 \neq H$, $R^3=Me$
(16) $R^1R^2=[CH_2]_4$, $R^3=H$
(17) $R^1=Et$, $R^2=R^3=Me$
(18) $R^1=CH_2Ph$, $R^2=Ph$, $R^3=Me$
(33) $R^1=R^2=Ph$, $R^3=Me$
(34) $R^1=Ph$, $R^2=H$, $R^3=Me$
(35) $R^1=Ph$, $R^2=R^3=Me$
(36) $R^1=H$, $R^2=Ph$, $R^3=Me$
(37) $R^1=H$, $R^2=R^3=Me$
(38) $R^1R^2=[CH_2]_4$, $R^3=Me$



(21) R = Et
(22) R = CH_2Ph
(39) R = Ph
(40) R = H
(42) R = $[CH_2]_4Me$



(24) R^1 and R^2 = H, alkyl, or aryl
(29) R^1 = Ph, R^2 = H
(31) R^1 = H, R^2 = alkyl

δ 8.0—9.86 due to the exchangeable NH, a singlet at 2.53—2.58 from the 6-methyl group, and a pair of doublets in each of the ranges 7.42—7.6 and 7.08—7.21 (J 8.5—9.7 Hz) caused by the 4- and the 5-H, respectively.

[1] P. D. Cook and R. N. Castle, *J. Heterocyclic Chem.*, 1973, **10**, 807, and references therein.
[2] H. Lund and S. Gruhn, *Acta Chem. Scand.*, 1966, **20**, 2637.
[3] A. H. Kelly and J. Parrick, *Canad. J. Chem.*, 1966, **44**, 2455.
[4] A. H. Kelly and J. Parrick, *J. Chem. Soc.* (*C*), 1970, 303.
[5] B. A. J. Clark, J. Parrick, and R. J. Dorgan, preceding paper.

Signals from these ring protons were assigned on the basis of evidence from the n.m.r. spectrum of cyclohexanone pyridazin-3-ylhydrazone (16), where the additional coupling made possible the assignment of the signal at 7.55 to the 4-H. It was clearly *meta*-coupled (J 1.5 Hz) to the lower field 6-H at 8.58, whereas the 5-H signal was at 7.23 ($J_{4,5}$ 9.0, $J_{5,6}$ 4.5 Hz). The i.r. spectra showed NH stretching peaks in the region 3 230—3 454 cm^{-1}.

azines (21) and (22) This formulation was confirmed by the i.r. spectra, which did not show an NH peak, and also the ^1H n.m.r. spectrum. This showed neither a peak removable by exchange with D_2O nor the singlet expected for the 4-H of (15), but did have the two doublets expected from the 7- and 8-H of (21) and (22). 3-Ethyl-6-methyl-*s*-triazolo[4,3-*b*]pyridazine prepared by the reaction of 3-hydrazino-6-methylpyridazine with propionic acid was identical with the product (21) from (17).

TABLE 1

6-Methylpyridazin-3-ylhydrazones

6-Methylpyridazin-3-yl-hydrazone of	M.p. (°C)	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N	ν_{NH}/cm^{-1}
Diethyl ketone (17)	(B.p. 130—131° at 0.3 mmHg)	59	62.7	8.3	29.0	$C_{10}H_{16}N_4$	62.5	8.3	29.2	3 230
Dibenzyl ketone (18)	127—129 [a]	74	75.6	6.4	17.7	$C_{20}H_{20}N_4$	75.9	6.3	17.7	3 450
Benzyl phenyl ketone (33)	152—153.5 [b]	44	75.7	6.1	18.6	$C_{19}H_{18}N_4$	75.5	6.0	18.5	3 430
Acetophenone (34)	159.5—161.5 [b]	86	68.8	6.0	24.4	$C_{11}H_{13}N_4$	69.0	6.3	24.7	3 400
Propiophenone (35)	132—134 [c]	58	70.4	6.5	23.1	$C_{14}H_{16}N_4$	70.0	6.7	23.3	3 450
Phenylacetaldehyde (36)	149—150 [a]	66	69.0	6.4	24.6	$C_{13}H_{14}N_4$	69.0	6.2	24.8	3 408
Propionaldehyde (37)	102—104 [d]	57	58.4	7.2	33.9	$C_8H_{12}N_4$	58.4	7.3	34.1	3 464
Cyclohexanone (38)	117—119 [e]	88	64.5	7.7	27.4	$C_{11}H_{16}N_4$	64.8	7.9	27.4	3 290
Pyridazin-3-ylhydrazone of cyclohexanone (16)	131—132.5 [d]	58	63.3	7.3	29.4	$C_{10}H_{14}N_4$	63.2	7.4	29.5	3 190

[a] From light petroleum (b.p. 80—100°). [b] From carbon tetrachloride. [c] From light petroleum (b.p. 60—80°). [d] From carbon tetrachloride–light petroleum (b.p. 40—60°). [e] From cyclohexane.

TABLE 2

^1H n.m.r. spectra (δ values; J in Hz; solvent $CDCl_3$) of pyridazinylhydrazones

Hydrazone	H-4 [a]	H-5 [a]	$J_{4,5}$	NH [b]	R^1	R^2	CH_2	R^3
(17)	7.42	7.12	9.5	8.0	2.32 (2 H, q, J 7, CH_2) 1.17 (3 H, t, J 7, CH_3)	1.17 (3 H, t, J 7, CH_3)	2.32 [c] (q, J 7)	2.55 [d]
(18)	7.46	7.08	9.7	9.2	7.25 (5 H, m, Ph) 3.65 (2 H, s, CH_2)	7.25 (5 H, m, Ph)	3.65 [c] (s)	2.53 [d]
(33)	7.45	7.21	8.5	8.65	7.51 (5 H, m, Ph)	7.51 (5 H, m, Ph)	4.18 [c] (s)	2.56 [d]
(34)	7.60	7.18	9.0	8.3	7.51 (5 H, m, Ph)	2.31 (3 H, s, CH_3)		2.58 [d]
(35)	7.60	7.17	9.1	8.9	7.57 (5 H, m, Ph)	1.18 (3 H, t, J 8.5, CH_3)	3.07 [c] (q, J 8.5)	2.57 [d]
(36)	7.46	7.11	9.35	9.36	7.80 (1 H, t, J 6.5)	7.30 (5 H, m, Ph)	3.68 [c] (d, J 6.5)	2.53 [d]
(37)	7.46	7.16	9.0	9.86	7.68 (1 H, t, J 5.0)	1.17 (3 H, t, J 8.0, CH_3)	2.33 [c] (m)	2.55 [d]
(38)	7.46	7.13	9.0	8.0	1.68 (6 H, m, 3 × CH_2) and 2.40 (4 H, m, 2 × CH_2)			2.55 [d]
(16)	7.55 [e]	7.23 [f]	9.0	8.36	1.70 (6 H, m, 3 × CH_2) and 2.41 (4 H, m, 2 × CH_2)			8.58 [g]

[a] 1 H, d. [b] 1 H, br, s, exchanged with D_2O. [c] 2 H. [d] 3 H, s, CH_3. [e] 1 H, q, $J_{4,6}$ 1.5. [f] 1 H, q, $J_{5,6}$ 4.5. [g] 1 H, q, J 4.5 and 1.5.

The thermal cyclisation of the 6-methylpyridazin-3-ylhydrazones was initially attempted in refluxing diethylene glycol (a solvent found satisfactory in other cases [3-5]), but this polar solvent caused difficulties in t.l.c. analysis of the reaction mixtures, and made isolation of the products troublesome. Tetralin was a more satisfactory solvent, and t.l.c. analysis showed that the same products were present in the reaction mixtures when either diethylene glycol or tetralin was used. The reaction was continued until the spot due to the hydrazone disappeared and, after removal of the solvent, the product was subjected to preparative t.l.c. A number of bands, fluorescent under u.v. light, were obtained from each reaction mixture, but in most cases only the major fluorescent band yielded sufficient material for identification.

The hydrazones from diethyl and dibenzyl ketone [(17) and (18), respectively] each yielded one isolable product. The elemental analysis results did not agree with the expected pyrrolo[2,3-*c*]pyridazine structures [(19) and (20)], but were acceptable for the *s*-triazolo[4,3-*b*]pyrid-

[6] T. D. Duffy and D. G. Wibberley, *J.C.S. Perkin I*, 1974, 1921.

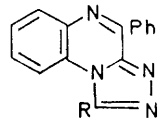
These results were unexpected, since in all other thermal cyclisations of a monocyclic heteroarylhydrazone, where cyclisation could theoretically occur on either an adjacent nitrogen or an adjacent carbon atom [(10), (11), and (23)], the product isolated has been formed by ring closure on to carbon,[3,5,6] and there is no clear t.l.c. evidence for by-products caused by reaction at the ring nitrogen atom in these cases.

When the heteroaryl nucleus is bicyclic, and where cyclisation from a 2- to a 3-position is unlikely [7] and is, in any event, blocked by a substituent, *e.g.* in hydrazones from 2-hydrazino-3-phenylquinoxaline (24), *s*-triazoloquinoxalines (25) have been obtained, one of the groups R^1 or R^2 being preferentially eliminated as a hydrocarbon (R^1H or R^2H).[8] A later attempt to repeat and extend this work with 2-quinoxalyl-, 2-pyridyl-, pyrazin-2-yl-, and 2-quinolyl-hydrazones was unsuccessful; [9] the quin-

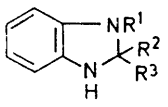
[7] B. Robinson, *Chem. Rev.*, 1963, **63**, 373.
[8] D.-I. Shiho and S. Tagami, *J. Amer. Chem. Soc.*, 1960, **82**, 4044.
[9] K. T. Potts and S. W. Schneller, *J. Heterocyclic Chem.*, 1968, **5**, 485.

oxalylhydrazones were recovered and no cyclisation products were isolated from any of the four types of heteroarylhydrazine investigated.

Earlier studies [10] of the condensation of *N*-substituted phenylenediamines with aliphatic ketones had given



(25) R = alkyl or aryl
(28) R = Ph
(30) R = alkyl



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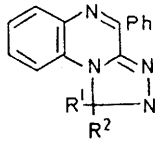

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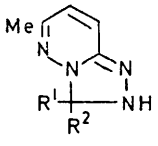

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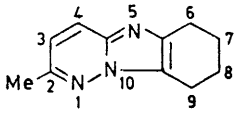

(43)

1,2,2-trisubstituted 2,3-dihydrobenzimidazole (26) which, on further heating, gave 2-substituted benzimidazoles and an alkane, by what was thought to be a base-catalysed fission of the C–C bond. It was suggested [8] that in a similar way the quinoxalylhydrazones gave an intermediate disubstituted dihydrotriazoloquinoxaline (27), which then subsequently eliminated the hydrocarbon to give (25). Elderfield and McCarthy [10] determined an order for the ease of elimination of alkyl groups from (26), in which isopropyl and ethyl were lost more readily than the methyl group. The findings [8] in the quinoxaline series agreed with this order, with the addition that phenyl derivative (28) was obtained from the acetophenone hydrazine (29), and the alkyl group was retained (30) from aliphatic aldehyde hydrazones (31). It seemed likely that cyclisation occurred before elimination in the reaction of pyridazinylhydrazones, and that a corresponding intermediate (32) and elimination process was involved in the formation of the *s*-triazolopyridazine. The two examples investigated initially involved symmetrical ketones and would give an intermediate (32), where $R^1 = R^2$. It was of interest to cyclise hydrazones which would lead to the intermediate with $R^1 \neq R^2$.

6-Methylpyridazin-3-ylhydrazones from benzyl phenyl ketone (33), acetophenone (34), propiophenone (35), phenylacetaldehyde (35), and propionaldehyde (37) were prepared (Table 1) and subjected to thermal cyclisation, and the products were isolated by preparative t.l.c. All these were *s*-triazolo[4,3-*b*]pyridazines: the first three hydrazones yielded the same product, 6-methyl-3-phenyl-*s*-triazolo[4,3-*b*]pyridazine (39), and the phenylacetaldehyde hydrazone (35) yielded the 3-unsubstituted derivative (40). Thus a benzyl group was eliminated more readily than phenyl or hydrogen, and also a methyl or an ethyl group was lost more easily than the phenyl residue. The propionaldehyde hydrazone gave two products: the 6-methyl- (40) and the 3-ethyl-6-methyl-triazolopyridazine (21), the latter being the major product and indicating that a hydrogen species is lost more readily than an alkyl group. Presumably the hydrogen species is not H^-, and this appears to indicate that the mechanism is of a radical type. The incomplete evidence from the ease of loss of organic groups does not conflict with this idea.

Some evidence that the eliminated group is lost as RH was obtained in the cyclisation of cyclohexanone 6-methylpyridazin-3-ylhydrazone (38). In this case the proposed intermediate would be the spiran (41), and expected rupture of the C–O bond would lead to the 6-methyl-3-pentyltriazolopyridazine (42). This compound was isolated (13%). However, a second major component (22%) of the reaction mixture had elemental analysis and mass spectral data which indicated the molecular formula $C_{11}H_{13}N_3$. The i.r. and n.m.r. spectra showed no evidence of NH bands, and the n.m.r. spectrum agreed with the 6,7,8,9-tetrahydro-2-methylpyridazino[2,3-*a*]benzimidazole structure (43).

Formation of (43) has again occurred by cyclisation at nitrogen but, this time, with elimination of a nitrogen atom—the latter being reminiscent of the thermal indolisation processes observed with phenyl- and some monocyclic heteroaryl-hydrazones. The factors which determine whether thermal cyclisation of a monocyclic heteroarylhydrazone will occur at the carbon or the nitrogen atom of the heterocycle and, in the latter case, whether the formally unsaturated carbon or the saturated α-carbon atom will be the site of the new ring junction are still unclear. The evidence indicates that the cyclisation, whether it be with concomitant loss of a carbon- or a nitrogen-containing fragment, preferentially occurs at the position adjacent to a ring nitrogen atom, irrespective of whether that position is occupied by a nitrogen or a carbon atom.

EXPERIMENTAL

I.r. spectra were obtained with a Unicam SP 200 spectrometer for KBr discs, and n.m.r. spectra with a Varian T60 instrument (tetramethylsilane as internal standard; solvent $CDCl_3$). 3-Hydrazino-6-methylpyridazine and 3-hydrazinopyridazine were prepared by the reactions of hydrazine hydrate with 3-chloro-6-methylpyridazine [11] and 3-chloropyridazine,[12] respectively.

Pyridazinylhydrazones (General Method).—The 3-hydrazinopyridazine and the ketone or aldehyde (1.2 mol. equiv.) were refluxed in toluene in the presence of a catalytic quantity of toluene-*p*-sulphonic acid. The reaction was

[10] R. C. Elderfield and J. R. McCarthy, *J. Amer. Chem. Soc.*, 1951, **73**, 975.

[11] D. Shiho and N. Takahayashi, *J. Pharm. Soc. Japan*, 1955, **75**, 776.

[12] S. Gabriel, *Ber.*, 1909, **42**, 654.

stopped when no more water had collected in the Dean–Stark trap (1—4 h), and the mixture was evaporated to dryness under reduced pressure. The residue was crystallised (Tables 1 and 2).

3-*Ethyl*-6-*methyl*-s-*triazolo*[4,3-b]*pyridazine* (21).—The 6-methylpyridazin-3-ylhydrazone of diethyl ketone (1 g) was refluxed in tetralin (30 ml) for 6 h, and the reaction was monitored by t.l.c. The tetralin was distilled off under reduced pressure and the residue was dissolved in chloroform and then separated by preparative t.l.c. on silica gel with acetone–light petroleum (b.p. 40—60°) (50 : 50 v/v) as eluant. Three major fluorescent bands were observed under u.v. light. Removal of these bands from the plate and their separate extraction with chloroform yielded only traces of material in two cases, but the band of lowest R_F (0.09) yielded a solid which was crystallised from water to give 3-*ethyl*-6-*methyl*-s-*triazolo*[4,3-b]*pyridazine* (0.25 g, 29%), m.p. 67—69° (Found: C, 59.4; H, 6.3; N, 34.4. $C_8H_{10}N_4$ requires C, 59.2; H, 6.2; N, 34.6%), δ 1.5 (3 H, t, *J* 8 Hz, CH_3), 2.6 (3 H, s, CH_3), 3.22 (2 H, q, *J* 8 Hz, CH_2), 6.95 (1 H, d, *J* 9.5 Hz, 7-H), and 7.98 (1 H, d, *J* 9.5 Hz, 8-H).

The same compound (identical m.p. and i.r. and n.m.r. spectra) was obtained (72%) when 3-hydrazino-6-methylpyridazine (1 g) in propionic acid (10 ml) was refluxed for 2 h, the excess of propionic acid was removed under reduced pressure, and the residue was crystallised from water.

3-*Benzyl*-6-*methyl*-s-*triazolo*[4,3-b]*pyridazine* (22).—In a similar way, the 6-methylpyridazin-3-ylhydrazone of dibenzyl ketone (2 g) in tetralin (60 ml) gave a component (R_F 0.26) which yielded 3-*benzyl*-6-*methyl*-s-*triazolo*[4,3-b]*pyridazine* (0.57 g, 39%), m.p. 130—131° (from carbon tetrachloride) (Found: C, 69.6; H, 5.3; N, 24.8. $C_{13}H_{12}N_4$ requires C, 69.6; H, 5.4; N, 25.0%), δ 2.53 (3 H, s, CH_3), 4.53 (2 H, s, CH_2), 6.87 (1 H, d, *J* 9.5 Hz, 7-H), 7.3 (5 H, m, Ph), and 7.9 (1 H, d, *J* 9.5 Hz, 8-H).

6-*Methyl*-3-*phenyl*-s-*triazolo*[4,3-b]*pyridazine* (39).—Similarly, when the 6-methylpyridazin-3-ylhydrazones of benzyl phenyl ketone, acetophenone, and propiophenone were separately refluxed in tetralin (7 h), the preparative chromatogram contained one component (R_F 0.45) that was isolated and crystallised from carbon tetrachloride to yield 6-*methyl*-3-*phenyl*-s-*triazolo*[4,3-b]*pyridazine* (66, 46, and 33%, respectively), m.p. 158.5—159.5° (Found: C, 68.7; H, 4.9; N, 26.7. $C_{12}H_{10}N_4$ requires C, 68.6; H, 4.8; N, 26.7%), δ 2.63 (3 H, s, CH_3), 6.98 (1 H, d, *J* 9.5 Hz, 7-H), 7.57 (3 H, m, ArH), 8.05 (1 H, d, *J* 9.5 Hz, 8-H), and 8.52 (2 H, m, Ar).

6-*Methyl*-s-*triazolo*[4,3-b]*pyridazine* (40).—When the 6-methylpyridazin-3-ylhydrazone of phenylacetaldehyde (1 g) was refluxed (7 h) in tetralin (30 ml), and the product was separated by t.l.c., the component of R_F 0.19 was purified by sublimation (125—130° at 0.5 mmHg) to give 6-methyl-s-triazolo[4,3-*b*]pyridazine (0.4 g, 60%), m.p. 157—159° (lit.,[13] 157—159°; lit.,[14] 166—168°), identical (m.p. and i.r. spectrum) with the product obtained (77%) when 3-hydrazino-6-methylpyridazine was refluxed (2 h) in formic acid.

Thermal Cyclisation of Propionaldehyde 6-*Methylpyridazin*-3-*ylhydrazone*.—The hydrazone (1.8 g) was refluxed in tetralin (30 ml) for 7 h, the tetralin was distilled off under reduced pressure, and the residue was dissolved in carbon tetrachloride. Preparative t.l.c. on silica gel with benzene–ethyl acetate (80 : 20 v/v) yielded a component (R_F 0.24) which crystallised from dioxan to yield 6-methyl-s-triazolo-[4,3-*b*]pyridazine (0.15 g, 10%), m.p. 157—159°, and a second component (R_F 0.49) which crystallised from water to give 3-ethyl-6-methyl-s-triazolo[4,3-*b*]pyridazine (0.37 g, 21%), m.p. 67—69°. Both products were identical with authentic samples.

6-*Methyl*-3-*pentyl*-s-*triazolo*[4,3-b]*pyridazine* (42) *and* 6,7,-8,9-*Tetrahydro*-2-*methylpyridazino*[2,3-a]*benzimidazole* (43).—Cyclohexanone 6-methylpyridazin-3-ylhydrazone (3 g) was refluxed in tetralin for 7 h, the tetralin was then removed, and the residue was extracted with hot cyclohexane. The extract gave, on evaporation, a residue (1.5 g) which was subjected to preparative t.l.c. (silica gel; 95 : 5 v/v chloroform–butan-1-ol). Two major bands of similar R_F value, both having a blue fluorescence under u.v. light, were formed. The band of R_F 0.52 was extracted with chloroform and the product distilled to give 6-*methyl*-3-*pentyl*-s-*triazolo*[4,3-b]*pyridazine* (0.4 g, 13%), b.p. 160—165° (bath temp.) at 0.4 mmHg (Found: C, 64.3; H, 7.8; N, 27.3. $C_{11}H_{16}N_4$ requires C, 64.7; H, 7.8; N, 27.3%), δ 0.93 (3 H, t, *J* 6 Hz, CH_3), 1.43 (4 H, m, 2 × CH_2), 1.9 (2 H, m, CH_2), 2.63 (3 H, s, CH_3), 3.2 (2 H, t, *J* 8 Hz, CH_2), 7.0 (1 H, d, *J* 9.5 Hz, 7-H), and 7.98 (1 H, d, *J* 9.5 Hz, 8-H).

The second band (R_F 0.48) was extracted with chloroform and the product sublimed at 120—124° (bath temp.) and 0.3 mmHg to give 6,7,8,9-*tetrahydro*-2-*methylpyridazino*-[2,3-a]*benzimidazole* (0.6 g, 22%), m.p. 74.5—76° (Found: C, 70.7; H, 7.1; N, 22.4. $C_{11}H_{13}N_3$ requires C, 70.6; H, 7.0; N, 22.5%), δ 1.98 (4 H, m, 2 × CH_2), 2.6 (3 H, s, CH_3), 2.92 (4 H, m, 2 × CH_2), 6.8 (1 H, d, *J* 9 Hz, 3-H), and 7.73 (1 H, d, *J* 9 Hz, 4-H).

[5/2064 *Received*, 22*nd October*, 1975]

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