Pyridazines. Part III.[1] Reaction of Di- and Tri-chlorodialkylaminopyridazines with Nucleophiles

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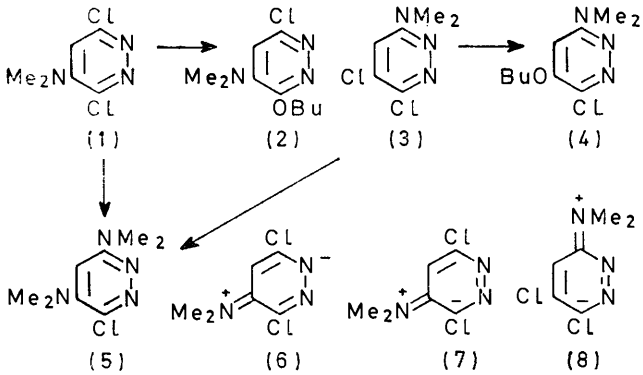
3,6-Dichloro-4-dialkylaminopyridazines on treatment with alkoxides give 3-alkoxy-6-chloro-4-dialkylaminopyridazines and with secondary amines give 4,6-diamino-3-chloropyridazine derivatives. Both alkoxides and amines substitute 3,4-dichloro-6-dimethylaminopyridazine at position 4, and 3,4-dichloro-5-dialkylaminopyridazines at position 3. Nucleophilic replacement reactions of trichlorodialkylaminopyridazines are usually non-selective.

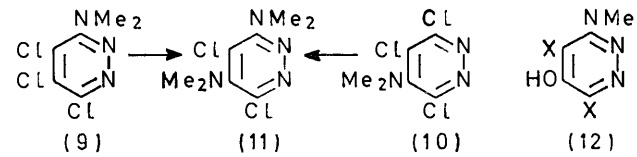
In Part II [1] we showed that nucleophilic attack by sodium butoxide on 3,6-dichloro-4-dimethylaminopyridazine (1) occurred at the 3-position, giving 3-butoxy-6-chloro-4-dimethylaminopyridazine (2), whereas with 3,4-dichloro-6-dimethylaminopyridazine (3) attack occurred at the 4-position, giving 4-butoxy-3-chloro-6-dimethylaminopyridazine (4). The generality of these reactions has been shown with other alcohols and with other 3,6-dichloro-4-dialkylaminopyridazines. The structures of the products were established by hydrogenolysis and determination of the n.m.r. coupling constants of the aromatic protons.



When 3,6-dichloro-4-dialkylaminopyridazines reacted with amines, however, substitution occurred at the 6-position giving, *e.g.*, 3-chloro-4,6-bisdimethylaminopyridazine (5) and 3-chloro-4,6-dimorpholinopyridazine. Hydrogenolysis of these compounds gave 3,5-bis-(substituted amino)pyridazines, whose structures were confirmed by n.m.r. spectrometry. Further proof of 6-substitution was given by the preparation of 3-chloro-4,6-bisdimethylaminopyridazine from dimethylamine and 3,4-dichloro-6-dimethylaminopyridazine.

In 3,6-dichloro-4-dialkylaminopyridazines the lone electron pair on the exocyclic nitrogen atom should deactivate the 6-position by diminishing the double-bond character of the C(6)–N(1) bond (6). The alternative resonance form (7) which would deactivate position 3 is less likely to contribute to the state of the molecule because it increases the double bond character of the N(1)–N(2) bond; this involves an unfavourable interaction of the nitrogen lone pairs. Consideration of the degree of conjugation in the Wheland intermediates that may be postulated as transition states for 3- and 6-substitution also suggests that 3-substitution should occur. Reaction with alkoxides therefore follows the expected pattern, and attack of secondary amines at position 6 rather than 3 may be attributed to steric hindrance. In 3,4-dichloro-6-dialkylaminopyridazines the exocyclic lone pair has little influence on the relative reactivities of the chlorine atoms because the preference for a single bond between the nitrogen atoms makes resonance forms such as (8) improbable.

The reaction of dimethylamine with 3,4,5-trichloro-6-dimethylaminopyridazine (9) [1] or with 3,4,6-trichloro-5-dimethylaminopyridazine (10) [2] gave 3,5-dichloro-4,6-bisdimethylaminopyridazine (11), which was hydrogenolysed to give 3,5-bisdimethylaminopyridazine. With



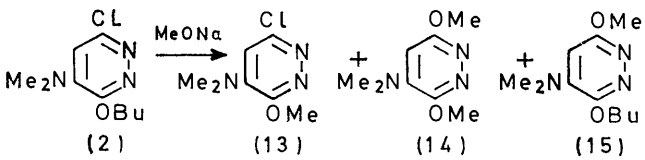
sodium alkoxides (1 equiv.), however, compounds (9) and (10) gave complex mixtures from which single components could rarely be isolated. When the reaction product from (9) and sodium ethoxide was treated with hydrogen chloride in ether one component was slowly converted into 3,5-dichloro-4-hydroxy-6-dimethylaminopyridazine (12; X = Cl), which was hydrogenolysed to 3-dimethylamino-5-hydroxypyridazine (12; X = H), in which the aromatic protons had a coupling constant of 2 Hz. From the reaction of 3,4,6-trichloro-5-morpholinopyridazine with sodium butoxide the 6-butoxy-derivative was isolated. On reduction this gave 3-butoxy-4-morpholinopyridazine, which was also obtained by a similar process from 3,6-dichloro-4-morpholinopyridazine.

3,4-Dichloro-5-morpholinopyridazine reacted both with sodium n-butoxide and with morpholine at the 3-position, and the resulting monochloro-compounds were reduced to give 3,5-disubstituted pyridazines.† This may be attributed either to steric hindrance or to deactivation of the 4-position by the amino-group. 3,4-Dichloro-5-dimethylaminopyridazine [3] with sodium n-butoxide gave the 3-butoxy-derivative.

† Proof of these structures was provided by the unambiguous synthesis of 5-butoxy-3-morpholinopyridazine (Part IV, in preparation).

[1] R. S. Fenton, J. K. Landquist, and Miss S. E. Meek, *J. Chem. Soc.* (*C*), 1971, 1536.
[2] R. Schönbeck and E. Kloimstein, *Monatsh.*, 1968, **99**, 15.
[3] I. Crossland and H. Kofod, *Acta Chem. Scand.*, 1967, **21**, 2131.

The remaining chlorine atoms in the foregoing diaminochloro- and alkoxyaminochloro-pyridazines were replaced by alkoxy-groups by treatment with sodium alkoxides, usually at higher temperatures (140—160°). When preparation of dialkoxy-compounds containing two different alkoxy-groups was attempted extensive alkoxy-group interchange was observed. Thus 3-butoxy-6-chloro-4-morpholinopyridazine with sodium n-propoxide gave only 4-morpholino-3,6-di-n-propoxypyridazine, and 3-butoxy-6-chloro-4-dimethylaminopyridazine (2) with sodium methoxide gave 6-chloro-4-dimethylamino-3-methoxypyridazine (13), 4-dimethyl-



amino-3,6-dimethoxypyridazine (14), and 3-butoxy-4-dimethylamino-6-methoxypyridazine (15). The presence of a chlorine substituent was necessary for this interchange: 4-morpholino-3,6-dipropoxypyridazine was recovered unchanged after being heated with sodium n-butoxide. Replacement of the last chlorine atom by an amino-group did not occur readily; conversion of 3-chloro-4,6-dimorpholinopyridazine into 3,4,6-trimorpholinopyridazine was incomplete after prolonged heating at 200°.

EXPERIMENTAL

Reaction of Polychloropyridazines with Morpholine.— 3,4,6-Trichloropyridazine (7·0 g) and morpholine (6·0 ml) in benzene (100 ml) were boiled under reflux for 4 h and the solvent was evaporated. The residue was extracted with boiling light petroleum (b.p. 100—120°) and the extracts on cooling gave crystals (7·5 g) of 3,6-*dichloro*-4-*morpholinopyridazine*, m.p. 114—115° (Found: C, 41·3; H, 3·9; N, 18·0. $C_8H_9Cl_2N_3O$ requires C, 41·0; H, 3·8; N, 18·0%). In a similar manner 3,4,5-trichloropyridazine and 3,4,5,6-tetrachloropyridazine gave 3,4-*dichloro*-5-*morpholinopyridazine*, m.p. 109° (Found: C, 41·3; H, 4·1; N, 17·9%), and 3,4,6-*trichloro*-5-*morpholinopyridazine*, m.p. 119° (Found: C, 36·0; H, 3·4; Cl, 39·4; N, 15·5. $C_8H_8Cl_3N_3O$ requires C, 35·7; H, 3·0; Cl, 39·6; N, 15·6%).

4-*Morpholinopyridazine.*— 3,4,6-Trichloro-5-morpholinopyridazine (2·0 g) in ethanol (15 ml) was hydrogenated over 5% palladium–carbon and the product was isolated as the *picrate*, m.p. 194—195° (Found: C, 43·0; H, 3·7; N, 20·9. $C_8H_{11}N_3O,C_6H_3N_3O_7$ requires C, 42·6; H, 3·6; N, 21·3%), τ[$(CD_3)_2SO$] 0·88 (d, *J* 4 Hz), 1·0 (d, *J* 8 Hz), 1·32 (s, picrate), 2·58 (q, *J* 4 and 8 Hz), and 6·25 (s).

Alkoxychlorodialkylaminopyridazines.— 3,4-Dichloro-5-morpholinopyridazine (3·0 g) was boiled for 10 h with a solution of sodium (0·3 g) in n-butanol (50 ml). The solvent was evaporated under reduced pressure and the residue was crystallised from light petroleum (b.p. 80—100°) to give 3-*n-butoxy*-4-*chloro*-5-*morpholinopyridazine* (3·2 g), m.p. 83—85° (Found: C, 52·7; H, 6·3; N, 15·4. $C_{12}H_{18}ClN_3O_2$ requires C, 53·0; H, 6·6; N, 15·5%). Hydrogenation of this compound (Pd–C in ethanol) gave 3-*n-butoxy*-5-*morpholinopyridazine hydrochloride*, which crystallised from butanone as the hydrate, m.p. 122° (Found: C, 49·6; H, 7·5; Cl, 12·0; N, 14·3. $C_{12}H_{19}N_3O_2,HCl,H_2O$ requires C, 49·4; H, 7·5; Cl, 12·2; N, 14·4%), coupling constant for aromatic protons 2·5 Hz. Other monoalkoxy-derivatives made similarly are listed in Tables 1 and 2.

3,5-*Diaminopyridazine Derivatives.*—3-*Chloro*-4,6-*bisdimethylaminopyridazine.* (*a*) 3,6-Dichloro-4-dimethylaminopyridazine (2·3 g) and ethanol saturated with dimethylamine (40 ml) were heated at 140° for 6 h in a sealed tube. The solvent was evaporated and the residue was extracted with boiling light petroleum (b.p. 80—100°; 2 × 100 ml). The petroleum was evaporated and the residual oil (2·5 g) was dissolved in ether and treated with hydrogen chloride to give the *hydrochloride*, m.p. 218—220° (from ethanol) (Found: C, 40·5; H, 6·1; Cl, 29·4; N, 23·4. $C_8H_{13}ClN_4,HCl$ requires C, 40·5; H, 5·9; Cl, 29·9; N, 23·6%).

(*b*) 3,4-Dichloro-6-dimethylaminopyridazine (1 g) and ethanolic dimethylamine under the same conditions gave an identical hydrochloride (0·9 g), m.p. and mixed m.p. 218—219°.

3,5-*Dichloro*-4,6-*bisdimethylaminopyridazine.* Dimethylamine was passed into a solution of 3,4,5-trichloro-6-dimethylaminopyridazine (3 g) in dry benzene (100 ml) until the mildly exothermic reaction was complete (2 h). The solution was filtered from dimethylamine hydrochloride and was evaporated. The *product* crystallised from cyclohexane as platelets, m.p. 58° (Found: C, 41·2; H, 5·7; Cl, 30·4; N, 24·2. $C_8H_{12}Cl_2N_4$ requires C, 40·85; H, 5·1; Cl, 30·2; N, 23·8%). The same product was obtained by prolonged reaction of tetrachloropyridazine with dimethylamine in benzene (the initial product is 3,4,6-trichloro-5-dimethylaminopyridazine) or in ethanol.

Hydrogenation of 3,5-dichloro-4,6-bisdimethylaminopyridazine or 3-chloro-4,6-bisdimethylaminopyridazine (Pd–C in ethanol) gave 3,5-*bisdimethylaminopyridazine hydrochloride*, m.p. 259—260° (Found: C, 43·5; H, 7·5; Cl, 16·2; N, 25·1. $C_8H_{14}N_4,HCl,H_2O$ requires C, 43·5; H, 7·7; Cl, 16·1; N, 25·4%), τ [$(CD_3)_2SO$] 1·65 (d) and 4·0 (d) (*J* 2 Hz), and 6·8 (s).

3-*Chloro*-4,6-*dimorpholinopyridazine.* 3,6-Dichloro-4-morpholinopyridazine (1 g), morpholine (6 ml), and benzene (25 ml) were boiled under reflux for 40 h and the solvent and excess of morpholine were evaporated. The residue was extracted with light petroleum (b.p. 80—100°) and the extract was evaporated. Crystallisation from cyclohexane gave the *product*, m.p. 175—176° (Found: C, 50·5; H, 6·1; N, 19·8. $C_{12}H_{17}ClN_4O_2$ requires C, 50·6; H, 6·0; N, 19·7%).

4-*Chloro*-3,5-*dimorpholinopyridazine.* 3,4-Dichloro-5-morpholinopyridazine (1·7 g) and morpholine (3 ml) were heated at 95—100° for 4 h and the excess of morpholine was evaporated. The residue was shaken with benzene and dilute sodium hydroxide solution and the benzene layer was dried (Na_2SO_4) and evaporated. Crystallisation from cyclohexane gave the *product*, m.p. 152—153° (Found: C, 50·5; H, 6·0; N, 19·8%), τ ($CDCl_3$) 1·43 (s, 1H), 6·15 (m, 8H), and 6·7 (m, 8H). Hydrogenation of both the chloro-dimorpholino-derivatives gave 3,5-*dimorpholinopyridazine hydrochloride*, m.p. 258—260° (from ethanol) (Found: C, 50·5; H, 6·8; N, 19·8. $C_{12}N_{17}N_4O_2,HCl$ requires C, 50·3; H, 6·6; N, 19·5%), τ [$(CD_3)_2SO$] 1·38 (d) and 3·34 (d) (*J* 4 Hz), and 6·23 (s).

3,4,6-*Trimorpholinopyridazine.* 3,6-Dichloro-4-morpholinopyridazine (2 g) and morpholine (35 ml) were heated in a sealed tube at 200° for 16 h, the excess of morpholine was evaporated, and the residue was treated with water. The insoluble solid (1·5 g) was separated by preparative t.l.c. (silica; EtOAc–EtOH, 10 : 1) into 3-chloro-4,6-dimorpholinopyridazine (0·4 g) and the *trimorpholino-compound* (0·9 g), m.p. 199—201° (from ethyl acetate) 4·1 (s, 1H), 5·7—5·8 (d, 2H), 6·7 (s, 6H), 6·8 (s, 6H), and 8·0—9·5 (m, 7H).

Dialkoxydialkylaminopyridazines.—A solution of sodium (1 equiv.) in the requisite alcohol was heated with alkoxychlorodialkylaminopyridazine (1 equiv.) or dichlorodialkylaminopyridazine (0·5 equiv.) under reflux for 6—24 h (method A), or in a sealed tube at 160° for 12—18 h (method B), or the sodium alkoxide and chloro-compound were

TABLE 1

3-Alkoxy-4-dialkylaminopyridazines

Substituent at position 3	4	6	Formula	M.p. (°C)	Found (%) C	H	Cl	N	Required (%) C	H	Cl	N	*J*/Hz [a]
MeO	Me_2N		$C_7H_{11}N_3O,HCl$ [b]	163—164	44·2	6·3	18·6	21·7	44·3	6·3	18·7	22·2	7
EtO·$[CH_2]_2$·O	Me_2N		$C_{10}H_{17}N_3O_2,HCl$	140—145	48·3	7·1	14·2	17·2	48·5	7·3	14·3	17·0	6·5
EtO·$[CH_2]_2$·O	Me_2N	Cl	$C_{10}H_{16}ClN_3O_2,HCl$	147—148	43·2	5·9	24·7	14·5	42·55	6·0	25·2	14·9	
Bu^nO	Morph [c]		$C_{12}H_{19}N_3O_2,HCl,H_2O$	167	49·9	7·5	12·8	14·5	49·4	7·5	12·2	14·4	7
Bu^nO	Morph	Cl	$C_{12}H_{18}ClN_3O_2$	68	53·0	6·6		15·8	53·0	6·6		15·5	
			$C_{12}H_{18}ClN_3O_2,HCl$	262—266	47·0	6·0		13·4	46·8	6·2		13·6	
EtO·$[CH_2]_2$·O	Morph		$C_{12}H_{19}N_3O_3,HCl$	192—193	50·0	7·0		14·5	49·7	6·9		14·5	6·5
EtO·$[CH_2]_2$·O	Morph	Cl	$C_{12}H_{18}ClN_3O_3$	104	49·6	6·5	12·5	14·4	50·1	6·3	12·3	14·6	

[a] Coupling constant of aromatic protons. [b] The free base was described by Crossland and Kofod.[4] [c] Morpholino.

TABLE 2

4-Alkoxy-6-dimethylaminopyridazines

Substituent at position 4	3	Formula	M.p. (°C)	Found (%) C	H	Cl	N	Required (%) C	H	Cl	N	*J*/Hz
MeO	Cl	$C_7H_{10}ClN_3O$	158—159	44·5	5·6	19·0	22·0	44·8	5·3	10·9	22·4	
MeO	H	$C_7H_{11}N_3O,HCl$	165—166	44·4	6·3	18·6	21·9	44·3	6·3	18·7	22·2	3
EtO	Cl	$C_8H_{12}ClN_3O$	102—103	48·0	5·9		20·7	47·6	6·0		20·8	
EtO	H	$C_8H_{13}N_3O,HCl$	181	47·3	6·7		20·1	47·3	6·9		20·6	
Pr^nO	Cl	$C_9H_{14}ClN_3O$	102—103	50·2	6·8		19·2	50·1	6·5		19·5	
Pr^nO	H	$C_9H_{15}N_3O,HCl,H_2O$	156—157	45·9	6·6		17·7	45·9	7·6		17·8	
EtO·C_6H_4·O	Cl	$C_{10}H_{16}ClN_3O_2$	71—73	49·0	6·4		17·1	48·9	6·5		17·1	
EtO·C_2H_4·O	H	$C_{10}H_{17}N_3O_2,HCl,H_2O$	136—137	45·1	6·8	13·4	15·6	45·2	7·5	13·4	15·8	2
n-$C_5H_{11}O$	Cl	$C_{11}H_{18}ClN_3O$	106	54·0	7·3		16·9	54·2	7·4		17·3	
n-$C_5H_{11}O$	H	$C_{11}H_{19}N_3O,HCl$	163—164	54·0	8·3		17·2	53·8	8·1		17·1	
n-$C_6H_{13}O$	Cl	$C_{12}H_{20}ClN_3O$	101	56·5	7·8		16·1	55·9	7·8		16·3	
n-$C_6H_{13}O$	H	$C_{12}H_{21}N_3O,HCl$	155	55·6	8·6		16·0	55·5	8·5		16·2	

TABLE 3

Dialkoxydialkylaminopyridazines

	Formula	M.p. (°C)	Method	Found (%) C	H	Cl	N	Required (%) C	H	Cl	N
3-Me_2N {5,6-$(Bu^nO)_2$	$C_{14}H_{25}N_3O_2,HCl$	155—157	B	55·4	8·5		13·9	55·4	8·6		13·8
3-Me_2N {5,6-(EtO·$[CH_2]_2$·O)$_2$	$C_{14}H_{25}N_3O_4,HCl,H_2O$	85—89 and 146—147	C	47·6	7·7	9·9	11·8	47·5	7·9	10·05	11·9
4-Me_2N {3,6-$(Bu^nO)_2$	$C_{14}H_{25}N_3O_2,HCl$	149—150	A	55·5	8·7	11·6	13·7	55·4	8·6	11·7	13·8
4-Me_2N {5,6-$(Bu^nO)_2$	$C_{14}H_{25}N_3O_2,HCl,0·5H_2O$	97	A	54·5	9·0		13·0	53·8	8·6		13·4
4-Me_2N {3,6(EtO·$[CH_2]_2$·O)$_2$	$C_{14}H_{25}N_3O_4,HCl,0·5H_2O$	129—130	A	49·0	8·0	10·2	12·2	48·8	7·8	10·3	12·2
4-Morph- {3,6-(Pr^nO_2)	$C_{14}H_{23}N_3O_3,HCl$	139	A	52·8	7·8		13·0	52·9	7·6		13·2
4-Morph- {3,6-$(Bu^nO)_2$	$C_{16}H_{27}N_3O_3,HCl$	134—135	A	55·2	8·0		12·5	55·6	8·1		12·2
4-Morph- {3,6-$(Bu^iO)_2$	$C_{16}H_{27}N_3O_3,HCl$	147—148	A	55·4	8·1		12·2				

(Found: C, 57·2; H, 7·4; N, 20·7. $C_{16}H_{25}N_5O_3$ requires C, 57·3; H, 7·5; N, 20·9%).

3-*n-Butoxy*-4,6-*bisdimethylaminopyridazine.* 3-Chloro-4,6-bisdimethylaminopyridazine (2·5 g) and a solution of sodium (0·55 g) in n-butanol (35 ml) were heated in a sealed tube at 150° for 24 h; the solution was evaporated to dryness and the residue was extracted with ether. Addition of hydrogen chloride to the extract precipitated the *hydrochloride*, m.p. 194—195° (from butanone) (Found: C, 52·5; H, 8·5; Cl, 13·1; N, 20·6. $C_{12}H_{22}N_4O,HCl$ requires C, 52·5; H, 8·4; Cl, 12·9; N, 20·4%), τ (D_2O)

boiled in dimethylformamide for 1—6 h (method C). After evaporation of excess of solvent and treatment with water to remove sodium chloride the products were isolated as hydrochlorides by treatment with hydrogen chloride in dry ether and were crystallised from butanone or ethanol–ethyl acetate. The dialkoxy-compounds are listed in Table 3. 3-n-Butoxy-6-chloro-4-dimethylaminopyridazine (2) (1·5 g) and sodium (0·15 g) in methanol (40 ml) were heated in a sealed tube at 140° for 6 h, the solvent was evaporated and the product was extracted with benzene. The crude product was separated by preparative t.l.c.

(silica GF with 4 : 1 benzene–ethyl acetate) into four components which were identified by n.m.r. spectroscopy as 4-dimethylamino-3,6-dimethoxypyridazine [τ ($CDCl_3$) 4·0 (s, 1H), 6·0 (2s, 6H), and 7·0 (s, 6H)], 3-chloro-5-dimethylamino-6-methoxypyridazine,[4] *3-n-butoxy-4-dimethylamino-6-methoxypyridazine* [τ ($CDCl_3$) 4·05 (s, 1H), 5·58 (t, 2H), 6·05 (s, 3H), 7·05 (s, 6H), and 8·2—9·1 (m, 7H)], *hydrochloride*, m.p. 207—208° (Found: C, 50·2; H, 7·4; Cl, 13·1; N, 15·9. $C_{11}H_{19}N_3O_2$,HCl requires C, 50·5; H, 7·65; Cl, 13·6; N, 16·1%), and the starting material (2).

3-n-Butoxy-6-chloro-4-morpholinopyridazine was boiled under reflux with sodium n-propoxide in n-propanol for 6 h. The product was almost pure 4-morpholino-3,6-di-n-propoxypyridazine.

3,4,5-Trichloro-6-dimethylaminopyridazine (6 g) was boiled under reflux for 3 h with a solution of sodium (0·6 g) in ethanol (30 ml); the ethanol was evaporated and the residue was extracted with ethyl acetate. The extract was evaporated and the residue was treated with hydrogen chloride in ether, giving an oily precipitate that solidified after 24—48 h. Crystallisation from ethanol gave *3,5-dichloro-6-dimethylamino-4-hydroxypyridazine*, m.p. 228—230° (Found: C, 34·6; H, 3·3; Cl, 34·0; N, 19·9. $C_6H_7Cl_2N_3O$ requires C, 34·6; H, 3·4; Cl, 34·1; N, 20·2%). Hydrogenation of this compound over palladium–carbon in ethanol gave *3-dimethylamino-5-hydroxypyridazine hydrochloride*, m.p. 255° (decomp.) (Found: C, 41·2; H, 5·7; Cl, 20·5; N, 22·7. $C_6H_9N_3O$,HCl requires C, 41·0; H, 5·7; Cl, 20·2; N, 23·9%), τ [$(CD_3)_2SO$–$CDCl_3$] 1·7 (d) and 3·0 (d) (*J* 2 Hz), and 6·65 (t).

3,4,6-Trichloro-5-morpholinopyridazine (5·0 g) and a solution of sodium (0·8 g) in n-butanol (100 ml) were boiled under reflux for 48 h and the solvent was then evaporated. The residue was extracted with hot light petroleum (b.p. 100—120°) and the extract was evaporated. Chromatography of the residual oil on silica in benzene–ethyl acetate or benzene–chloroform gave a fraction (R_F 0·6 on GF plates with 4 : 1 benzene–ethyl acetate) that slowly crystallised. Crystallisation from light petroleum (b.p. 60—80°) gave *6-n-butoxy-3,4-dichloro-5-morpholinopyridine*, m.p. 77—78° (Found: C, 47·5; H, 5·6; N, 13·4. $C_{12}H_{17}Cl_2N_3O_2$ requires C, 47·1; H, 5·5; N, 13·7%). Hydrogenation of this compound gave *3-n-butoxy-4-morpholinopyridazine hydrochloride*, m.p. 167°, identical with a sample made from 3-butoxy-6-chloro-4-morpholinopyridazine (Table 1).

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[4] I. Crossland and H. Kofod, *Acta Chem. Scand.*, 1970, **24**, 751.