Polyhalogeno-aromatic Compounds. Part XXVIII.[1] Derivatives of Polyhalogenopyridine-4-thiols

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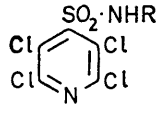
The tetrachloropyridine-4-sulphonamides (1)—(3) were prepared from tetrachloropyridine-4-sulphonyl chloride and allylamine, n-butylamine, or ethanolamine at low temperatures. Tetrachloropyridine-4-(*N*-2-hydroxyethyl)-sulphonamide (3) can undergo a double Smiles-type rearrangement (Scheme 1) on treatment with base at room temperature to give *N*-(tetrachloro-4-pyridyl)ethanolamine (4). Some reactions of 3,5-dichloro-2,6-difluoro- (7) and 2,3,5-trichloro-6-fluoro-pyridine-4-thiol (8) are reported.

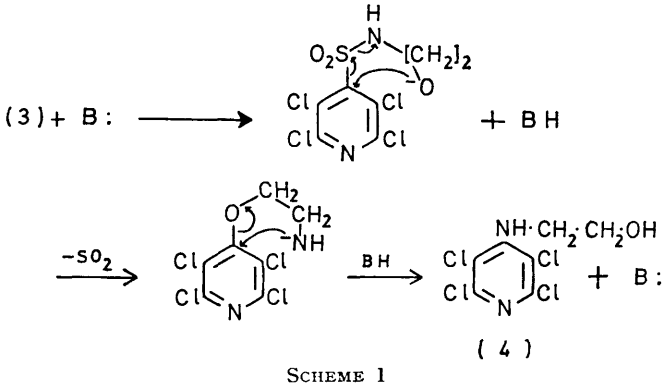
THE tetrachloropyridine-4-sulphonamides reported previously [2] possess fungicidal activity.[3] We now report further compounds of this type together with some reactions of 3,5-dichloro-2,6-difluoro- (7) and 2,3,5-trichloro-6-fluoro-pyridine-4-thiol (8).



(1) R = Bu^n
(2) R = $CH_2 \cdot CH{:}CH_2$
(3) R = $CH_2 \cdot CH_2 \cdot OH$

The sulphonamides (1)—(3) were prepared by reactions of tetrachloropyridine-4-sulphonyl chloride with n-butylamine (at 0° C), allylamine (at 0 °C), and ethanolamine (at −70 °C), respectively. Low temperatures are necessary for these reactions because amines can displace a sulphonamide group in analogous compounds at higher temperatures (see later).[2] When 2-aminopyridine was added to the sulphonyl chloride at −70 °C the product was 2(6)-pyridylammonium tetrachloropyridine-4-sulphonate, which arises presumably through hydrolysis of unchanged sulphonyl chloride to the corresponding sulphonic acid [2] during the work-up.

Treatment of tetrachloropyridine-4-sulphonyl chloride with a slight excess of ethanolamine at room temperature gave, unexpectedly, *N*-(tetrachloro-4-pyridyl)ethanolamine (4). This may arise in three ways: (i) by displacement of the preformed $SO_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot OH$ group with ethanolamine; (ii) by an S_Ni rearrangement of the sulphonamide (3), involving the side-chain nitrogen atom;



SCHEME 1

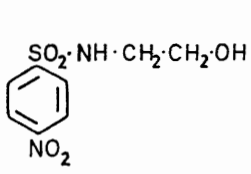
or (iii) by a double Smiles-type rearrangement, as shown in Scheme 1. The last pathway seemed a strong

[1] Part XXVII, J. Bratt and H. Suschitzky, *J.C.S. Perkin I*, 1973, 1689.

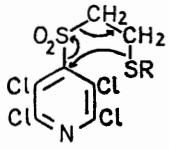
[2] E. Ager, B. Iddon, and H. Suschitzky, *J. Chem. Soc.* (*C*), 1970, 1530.

[3] C. D. S. Tomlin, B. Iddon, and E. Ager, B.P. 1,293,909/1972 (*Chem. Abs.*, 1973, **78**, 58,255).

possibility in view of the fact that *N*-(2-hydroxyethyl)-*p*-nitrobenzenesulphonamide (5) rearranges in the presence of dilute sodium hydroxide to give *N*-(*p*-nitrophenyl)-ethanolamine.[4] † Indeed, in keeping with this suggestion,



(5)



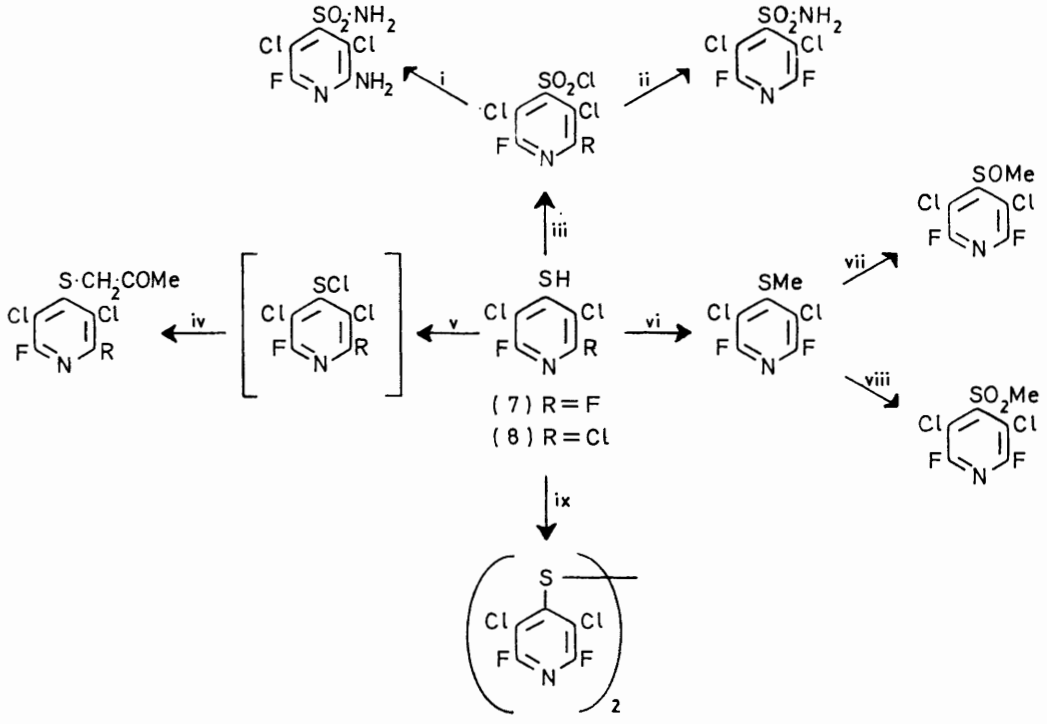
(6)

the sulphonamide (3) rearranged on treatment with triethylamine at room temperature, to give the ethanolamine derivative (4) in high yield. With n-butylamine, it gave a mixture of the ethanolamine derivative (4) (36·5%) and 4-*N*-n-butylaminotetrachloropyridine (22%). Treatment of the sulphonamide with sodium methoxide gave a mixture of products which contained the ethanolamine derivative (22%) and tetrachloro-4-methoxypyridine (25%). It seems likely therefore that the *N*-(tetrachloro-4-pyridyl)ethanolamine (4) which is formed on treatment of the sulphonyl chloride with ethanolamine arises as shown in Scheme 1, although direct displacement of the sulphonamide group by the ethanolamine present may account for some of the product.

† *Note added in proof:* the mechanism of this reaction has been discussed by A. C. Knipe (*Tetrahedron Letters*, 1973, 3031).

Since the completion of our work Moshchitskii *et al.*[5] have reported that the sulphones (6; R = C_6Cl_5) and (6; R = tetrachloro-4-pyridyl) rearrange on being heated to give tetrachloro-4-pyridyl pentachlorophenyl sulphide and bis(tetrachloro-4-pyridyl) sulphide, respectively.

Attempts to prepare tetrachloropyridine-4-sulphonohydrazide by reaction of tetrachloropyridine-4-sulphonyl chloride with hydrazine hydrate gave 2,3,5,6-tetrachloropyridine as the only isolable product, even when the reactions were carried out at low temperature. If the sulphonohydrazide is in fact formed, it could undergo a spontaneous rearrangement analogous to that shown in Scheme 1 to give tetrachloro-4-hydrazinopyridine, which is known [6] to decompose in the presence of base with nitrogen evolution to give 2,3,5,6-tetrachloropyridine. The intermediacy of the hydrazine was shown by addition of acetone to the reaction mixture prepared from the sulphonyl chloride and hydrazine, which gave small amounts (4—7%) of acetone tetrachloro-4-pyridylhydrazone.



SCHEME 2 Reagents: i, aq. NH_3 (R = F only); ii, Me_2CO–NH_3 (1 equiv.); iii, Cl_2–AcOH, then ice; iv, Me_2CO; v, Cl_2–CCl_4; vi, Me_2SO_4; vii, H_2O_2–AcOH; viii, H_2O_2–AcOH–conc. H_2SO_4; ix Br_2–AcOH

We also report the reactions of 3,5-dichloro-2,6-difluoro- (7) and 2,3,5-trichloro-6-fluoro-pyridine-4-thiol (8) shown in Scheme 2, which require no comment (see Experimental section). The sulphonyl chlorides were stable in air for long periods (see ref. 2). The starting

[4] K. G. Kleb, *Angew. Chem. Internat. Edn.*, 1968, **7**, 291.

[5] S. D. Moshchitskii, L. S. Sologub, Ya. N. Ivashchenko, and L. M. Yagupol'skii, *Khim. geterotsikl. Soedin.*, 1972, 1634 (*Chem. Abs.*, 1973, **78**, 71,864).

[6] I. Collins, S. M. Roberts, and H. Suschitzky, *J. Chem. Soc.* (*C*), 1971, 167.

materials, (7) and (8), were prepared by reaction of trichloro-2,6-difluoro- or tetrachloro-2(6)-fluoro-pyridine with sodium hydrogen sulphide;[7] the success of this procedure is surprising in view of the fact that these compounds react with nucleophiles generally by displacement of an α-fluorine atom.[8] With potassium benzenethiolate (2 mol. equiv.) trichloro-2,6-difluoropyridine gives a 2,4-disubstituted derivative.[1] These results are reminiscent of those of Davies *et al.*,[9] who found that the fluorine atom in 6-chloro-5-fluoro-1,2,3-benzothiadiazole is displaced preferentially by a hard nucleophile (*e.g.*, methoxide) whereas the chlorine atom is displaced preferentially by a soft nucleophile (*e.g.*, thiomethoxide). The most reactive halogen towards nucleophiles in 5,6-dichloro-1,2,3-benzothiadiazole is the 6-chlorine atom.

EXPERIMENTAL

Molecular weights were determined by mass spectrometry with an A.E.I. MS902S or MS12 instrument. All new compounds gave mass spectra with isotopic abundance ratios predicted for the numbers of chlorine atoms in them. I.r. spectra were recorded with a Perkin-Elmer 257 instrument and n.m.r. spectra with a Varian A60 spectrometer (tetramethylsilane as internal standard).

Light petroleum had b.p. 60—80 °C.

Reactions of Tetrachloropyridine-4-sulphonyl Chloride.—(a) *With n-butylamine.* The sulphonyl chloride (2·0 g, 6·3 mmol) was added in small portions to a stirred solution of the amine (0·93 g, 12·8 mmol) in ethanol (10 ml) at 0 °C and the resulting mixture was stirred at 0 °C for a further 30 min. The ethanol was distilled off under reduced pressure, water (10 ml) was added to the residue, and extraction with chloroform gave *tetrachloropyridine-4-(N-n-butyl)sulphonamide* (1) (1·8 g, 82%), m.p. 105—105·5 °C (from aqueous ethanol), $\nu_{max.}$ (Nujol) 3340 cm^{-1} (NH) (Found: C, 31·0; H, 2·9; N, 8·0%; *M*, 350. $C_9H_{10}Cl_4N_2O_2S$ requires C, 30·7; H, 2·9; N, 7·95%; *M*, 350).

(b) *With allylamine.* The reaction was carried out and the product worked up as described in (a) to give *tetrachloropyridine-4-(N-allyl)sulphonamide* (2) (1·7 g, 80%), m.p. 98·5—99 °C (from methanol), $\nu_{max.}$ (Nujol) 3340 cm^{-1} (NH) (Found: C, 28·9; H, 1·8; N, 8·3%; *M*, 334. $C_8H_6Cl_4N_2O_2S$ requires C, 28·6; H, 1·8; N, 8·3%; *M*, 334).

(c) *With 2-aminopyridine.* A solution of the sulphonyl chloride (5·0 g, 16·0 mmol) in ethanol (100 ml) was added dropwise to a solution of 2-aminopyridine (3·0 g, 32·0 mmol) in ethanol (100 ml) at −70 °C. The resulting mixture was stirred at −70 °C for a further 30 min and then allowed to warm slowly to room temperature. 2N-Hydrochloric acid (10 ml) was added, followed by water (20 ml), and the precipitate was filtered off, to give *2(6)-pyridylammonium tetrachloropyridine-4-sulphonate* (4·1 g, 66%), m.p. 199—200 °C (from ethanol), $\nu_{max.}$ (Nujol) 3200—3400br cm^{-1} ($\overset{+}{N}H_3$) (Found: C, 30·7; H, 1·9; N, 10·45. $C_{10}H_7Cl_4N_3O_3S$ requires C, 31·0; H, 1·8; N, 10·8%).

A mixture of a small amount of this salt and 4N-sodium hydroxide was kept overnight at room temperature. Extraction with ether gave 2-aminopyridine, identical (m.p. and i.r. spectrum) with an authentic sample. Evaporation of the aqueous layer to dryness, addition of concentrated hydrochloric acid to the residue, and extraction with ether gave tetrachloro-4-hydroxypyridine (see ref. 2), identical (m.p. and i.r. spectrum) with an authentic sample.

(d) *With ethanolamine.* (i) A solution of ethanolamine (0·76 g, 12·6 mmol) in ethanol (10 ml) was added dropwise to a stirred solution of the sulphonyl chloride (2·0 g, 6·3 mmol) in a mixture of chloroform (50 ml) and light petroleum (50 ml) at −70 °C. The resulting mixture was stirred for a further 30 min at −70 °C and then allowed to warm slowly to room temperature. Work-up as described in (a) gave *tetrachloropyridine-4-(N-2-hydroxyethyl)sulphonamide* (3) (2·0 g, 93%), m.p. 137·5—139 °C (from aqueous ethanol), $\nu_{max.}$ (Nujol) 3575 (OH) and 3295 cm^{-1} (NH) (Found: C, 24·8; H, 1·8; N, 8·3%; *M*, 338. $C_7H_6Cl_4N_2O_3S$ requires C, 24·7; H, 1·8; N, 8·2%; *M*, 338).

(ii) A solution of ethanolamine (0·6 g, 10·0 mmol) in benzene (25 ml) was added dropwise during 30 min to a stirred solution of the sulphonyl chloride (1·0 g, 3·2 mmol) in benzene (25 ml) at room temperature and the resulting mixture was stirred at this temperature for a further 30 min. Water (10 ml) was added and the organic layer was separated, dried ($MgSO_4$), and distilled to leave *N-(tetrachloro-4-pyridyl)ethanolamine* (4) (0·5 g, 57%), m.p. 126—127 °C (from ethanol) (lit.,[10] 126 °C), identical in all other respects with an authentic sample.

(e) *With hydrazine.* (i) A solution of the sulphonyl chloride (1·5 g, 4·75 mmol) in tetrahydrofuran (10 ml) was added dropwise during 15 min to a solution of hydrazine hydrate (0·6 g, 12·0 mmol) in water (2 ml) at 0 °C, and the resulting mixture was stirred at 0 °C for a further 15 min. It was then washed with saturated aqueous sodium chloride (2 × 30 ml) and dried ($MgSO_4$). An excess of acetone was added; distillation then left a white solid (1·15 g), which was chromatographed on silica. Light petroleum eluted 2,3,5,6-tetrachloropyridine (0·75 g, 73%), m.p. 89—90 °C (from aqueous methanol) (lit.,[6] 89 °C). Chloroform eluted *acetone tetrachloro-4-pyridylhydrazone* (0·1 g, 7%), m.p. 136—136·5 °C (from ethanol), $\nu_{max.}$ (Nujol) 3350 (NH) and 1375 cm^{-1} (CMe_2) (Found: C, 34·0; H, 2·5; N, 14·2%; *M*, 284·9392. $C_8H_7Cl_4N_3$ requires C, 33·5; H, 2·45; N, 14·6%; *M*, 284·9394).

(ii) A solution of hydrazine hydrate (1·6 g, 32·0 mmol) in ethanol (15 ml) was added dropwise to a stirred solution of the sulphonyl chloride (5·0 g, 15·8 mmol) in chloroform (30 ml) at −70 °C and the resulting mixture was kept at −70 °C for a further 30 min. Work-up as described before gave 2,3,5,6-tetrachloropyridine (1·7 g, 49·5%) and acetone tetrachloro-4-pyridylhydrazone (0·2 g, 4%).

Reactions of Tetrachloro-4-pyridyl-(N-2-hydroxyethyl)-sulphonamide (3).—(a) *With triethylamine.* A solution of triethylamine (0·15 g, 1·5 mmol) in ethanol (10 ml) was added to a stirred solution of the sulphonamide (3) (0·5 g, 1·5 mmol) in ethanol (10 ml) at room temperature and the resulting mixture was kept at room temperature overnight.

[7] C. D. S. Tomlin, J. W. Slater, D. Hartley, and C. J. Clayton, B.P. 1,059,990/1967; I.C.I. Ltd., Neth. P. Appl. 6,516,409/1966 (*Chem. Abs.*, 1966, **65**, 18,564).

[8] C. D. S. Tomlin, J. W. Slater, and D. Hartley, B.P. 1,161,492/1969 (*Chem. Abs.*, 1969, **71**, 91,313); I.C.I. Ltd., Neth. P. Appl. 6,611,766/1967 (*Chem. Abs.*, 1968, **68**, 59,438).

[9] J. H. Davies, E. Haddock, P. Kirby, and S. B. Webb, *J. Chem. Soc.* (*C*), 1971, 2843.

[10] M. K. N. Patel, M.Sc. Thesis, University of Salford, 1973.

The solvent was distilled off under reduced pressure and 2N-hydrochloric acid (5 ml) was added to the residue. Extraction with chloroform (3 × 10 ml) gave *N*-(tetrachloro-4-pyridyl)ethanolamine (4) (0·35 g, 85%), m.p. 127—128 °C (from ethanol), identical in all other respects with the sample prepared as described before.

(b) *With n-butylamine.* A reaction between the sulphonamide (3) (1·5 mmol) and n-butylamine (1·5 mmol) was carried out as described in (a). Work-up gave a solid (0·4 g) which was chromatographed on silica. Light petroleum–chloroform (7 : 3) eluted 4-*N*-n-butylaminotetrachloropyridine (0·1 g, 22%), b.p. 180 °C at 20 mmHg (Kugelrohr apparatus) (lit.,[11] 220° at 25 mmHg). Chloroform eluted *N*-(tetrachloro-4-pyridyl)ethanolamine (4) (0·15 g, 36·5%), m.p. 127—129 °C (from ethanol), identical with the samples prepared as described before.

(c) *With sodium methoxide.* A reaction between the sulphonamide (1·5 mmol) and sodium methoxide (1·5 mmol) was carried out in methanol (10 ml) as described in (a). The product (0·4 g) was chromatographed on silica. Light petroleum eluted tetrachloro-4-methoxypyridine (0·1 g, 25%), m.p. 116—118 °C (lit.,[12] 117—119 °C). Chloroform eluted *N*-(tetrachloro-4-pyridyl)ethanolamine (4) (0·1 g, 22%), m.p. 128—129 °C, identical with an authentic sample.

Reactions of Trichloro-2,6-difluoro- and Tetrachloro-2(6)-fluoro-pyridine with Sodium Hydrogen Sulphide.—(*a*) A solution of sodium hydroxide (1·0 g, 25·0 mmol) in water (20 ml) was saturated with hydrogen sulphide and then added dropwise to a stirred solution of trichloro-2,6-difluoropyridine (5·4 g, 25·0 mmol) in dioxan (50 ml) at 0 °C. The mixture was stirred at 0 °C for a further 1 h and then poured on ice (500 g). The resulting solution was acidified with concentrated hydrochloric acid. Extraction with ether gave an oil (4·0 g) which was distilled to give 3,5-dichloro-2,6-difluoropyridine-4-thiol (7) (3·29 g, 61%), m.p. 42—44 °C (lit.,[7] 44—46 °C). This compound was prepared similarly (80%) from 3,5-dichloro-2,4,6-trifluoropyridine.

(*b*) Tetrachloro-2(6)-fluoropyridine similarly gave 2,3,5-trichloro-6-fluoropyridine-4-thiol (8) (82%), m.p. 66—67 °C (from ethanol) (lit.,[7] m.p. 67—69 °C).

Bis-(3,5-dichloro-2,6-difluoro-4-pyridyl) disulphide (85%), m.p. 124—125 °C (from methanol) (Found: C, 28·3; N, 6·5. $C_{10}Cl_4F_4N_2S_2$ requires C, 27·9; N, 6·5%), was prepared from the thiol (7) by a procedure analogous to that described previously [2] for the synthesis of bis(tetrachloro-4-pyridyl) disulphide.

3,5-Dichloro-2,6-difluoropyridine-4-sulphonyl chloride (71%), prepared from the thiol (7) by a procedure analogous to that described previously [2] for the synthesis of tetrachloropyridine-4-sulphonyl chloride, had m.p. 68—69·5 °C (from light petroleum) (Found: C, 21·5; N, 5·0%; *M*, 281. $C_5Cl_3F_2NO_2S$ requires C, 21·3; N, 5·0%; *M*, 281).

2,3,5-Trichloro-6-fluoropyridine-4-sulphonyl chloride (86%), m.p. 68—69 °C (from light petroleum) (Found: C, 20·5; N, 4·8%; *M*, 297. $C_5Cl_4FNO_2S$ requires C, 20·1; N, 4·7%; *M*, 297), was prepared similarly from the thiol (8).

(3,5-Dichloro-2,6-difluoro-4-pyridylthio)acetone.— Dry chlorine was passed through a solution of 3,5-dichloro-2,6-difluoropyridine-4-thiol (7) (1·0 g, 4·6 mmol) in anhydrous acetic acid (100 ml) for 1 h. The resulting orange solution was poured into anhydrous acetone (25 ml). Removal of the solvents under reduced pressure gave the *product* (0·9 g, 71%), m.p. 131—132 °C (from carbon tetrachloride), $\nu_{max.}$ (Nujol) 1710 cm^{-1} (C:O), τ ($CDCl_3$) 6·02 (s, CH_2) and 7·67 (s, Me) (Found: C, 35·0; H, 2·0; N, 5·1%; *M*, 271. $C_8H_5Cl_2F_2NOS$ requires C, 35·3; H, 1·85; N, 5·15%; *M*, 271).

(2,3,5-Trichloro-6-fluoro-4-pyridylthio)acetone (82%), m.p. 93—94·5 °C (from carbon tetrachloride), $\nu_{max.}$ (Nujol) 1715 cm^{-1} (C:O) (Found: C, 33·25; H, 1·9; N, 4·8%; *M*, 287. $C_8H_5Cl_3FNOS$ requires C, 33·3; H, 1·75; N, 4·85%; *M*, 287), was prepared similarly from the thiol (8).

2-Amino-3,5-dichloro-6-difluoropyridine-4-sulphonamide.—3,5-Dichloro-2,6-difluoropyridine-4-sulphonyl chloride (0·8 g, 3·6 mmol) was added in small portions to aqueous ammonia (s.g. 0·88; 5 ml) at 0 °C. The mixture was stirred for 2 h at room temperature, filtered, and acidified with concentrated hydrochloric acid (7 ml) to give the *product* (0·61 g, 65%), m.p. 215—217 °C (from aqueous methanol) $\nu_{max.}$ (Nujol) 3340, 3380, and 3490 cm^{-1} (NH_2 and $SO_2{\cdot}NH_2$) (Found: C, 23·5; H, 1·7; N, 16·5%; *M*, 259. $C_5H_4Cl_2FN_3O_2S$ requires C, 23·1; H, 1·6; N, 16·2%; *M*, 259).

3,5-Dichloro-2,6-difluoropyridine-4-sulphonamide.— The sulphonyl chloride (3·0 g, 10·6 mmol) was added during 2 min to a stirred solution of aqueous ammonia (s.g. 0·88; 1 ml) in acetone (10 ml) at 0 °C and the resulting mixture was stirred at 0 °C for a further 5 min. The mixture was then filtered and the filtrate was acidified with concentrated hydrochloric acid (2 ml). Distillation of the acetone under reduced pressure gave a solid which was triturated with chloroform. Distillation of the combined chloroform washings gave the *product* (2·15 g, 76%), m.p. 170·5—172·5 °C (from aqueous ethanol), $\nu_{max.}$ 3310 and 3400 cm^{-1} ($SO_2{\cdot}NH_2$) (Found: C, 22·7; H, 0·9; N, 10·9%; *M*, 262. $C_5H_2Cl_2F_2N_2O_2S$ requires C, 22·8; H, 0·8; N, 10·65%; *M*, 262).

3,5-Dichloro-2,6-difluoro-4-methylsulphinylpyridine.— (i) Dimethyl sulphate (2·52 g, 20·0 mmol) was added to a stirred solution of 3,5-dichloro-2,6-difluoropyridine-4-thiol (7) (3·6 g, 16·7 mmol) in aqueous potassium hydroxide (5% w/v; 20 ml) at room temperature and the mixture was kept at room temperature overnight. The excess of dimethyl sulphate was destroyed with dilute aqueous ammonia; extraction with chloroform followed by distillation gave *3,5-dichloro-2,6-difluoro-4-methylthiopyridine* (3·1 g, 81%) as an oil, τ (CCl_4) 7·30 (s, Me) (Found: C, 31·1; H, 1·4; N, 6·2%; *M*, 229. $C_6H_3Cl_2F_2NS$ requires C, 31·3; H, 1·3; N, 6·1%; *M*, 229).

(ii) Hydrogen peroxide (30% w/v; 2 ml) was added to 3,5-dichloro-2,6-difluoro-4-methylthiopyridine (1·3 g, 5·6 mmol) in acetic acid (10 ml) at room temperature. The mixture was stirred overnight, then neutralised with aqueous sodium hydrogen carbonate. Extraction with chloroform gave an oil (1·4 g) which was chromatographed on silica. Chloroform eluted *3,5-dichloro-2,6-difluoro-4-methylsulphinylpyridine* (1·0 g, 72%), m.p. 107—108·5 °C (from methanol) (Found: C, 29·5; H, 1·4; N, 5·5%; *M*, 245. $C_6H_3Cl_2F_2NOS$ requires C, 29·3; H, 1·2; N, 5·7%; *M*, 245).

3,5-Dichloro-2,6-difluoro-4-methylsulphonylpyridine.— Hydrogen peroxide (30% w/v; 7 ml) was added to a cooled (0 °C), stirred solution of 3,5-dichloro-2,6-difluoro-4-methylthiopyridine (2·3 g, 10 mmol) in a mixture of acetic acid (20 ml) and concentrated sulphuric acid (10 ml); the resulting mixture was stirred overnight at room temperature, then poured on ice to give the product (2·2 g, 85%), m.p. 129—

[11] S. M. Roberts and H. Suschitzky, *J. Chem. Soc.* (*C*), 1968, 2844.

[12] A. Roedig, K. Grohe, and D. Klatt, *Chem. Ber.*, 1966, **99**, 2818.

130 °C (from methanol) (lit.,[13] 118—123 °C) (Found: C, 27·5; H, 1·3; N, 5·5%; *M*, 261. $C_6H_3Cl_2F_2NO_2S$ requires C, 27·5; H, 1·15; N, 5·3%; *M*, 261).

We thank Plant Protection Ltd. (PPL), Jealott's Hill, for a research studentship (to A. W. T.), Dr. C. D. S. Tomlin (PPL) and Dr. M. B. Green (I.C.I. Ltd., Mond Division, Runcorn Heath) for their interest and for gifts of various polyhalogenopyridines, and Mr. M. K. N. Patel (University of Salford) for an authentic sample of *N*-(tetrachloro-4-pyridyl)ethanolamine.

[3/1575 *Received*, 25*th July*, 1973]

[13] H. Johnston, U.S.P. 3,371,011/1968 (*Chem. Abs.*, 1968, **69**, 59,109).