Polyhalogenoaromatic Compounds. Part 50.[1] Reactions of 4-Benzyloxytetrahalogenopyridines with Nucleophiles **

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Reaction of 4-benzyloxy-3,5-dichloro-2,6-difluoro- (1; R = CH$_2$Ph) and 4-benzyloxytetrachloro-pyridine (2; R = CH$_2$Ph) with various nucleophiles (*N,N*-dimethylhydrazine, piperidine, *N,N,N',N'*-tetramethylethane-1,2-diamine, triphenylphosphine) occurs unexpectedly at the benzylic methylene group with alkyl–oxygen cleavage to give the corresponding benzylammonium (4) or triphenylphosphonium salt (9) respectively. The molecular structure of the salt derived from 4-benzyloxytetrachloro-pyridine and *N,N*-dimethylhydrazine was confirmed by an X-ray study. Preliminary experiments of utilising the benzyl cleavage for the preparation of various benzyl derivatives (PhCH$_2$X; X = Cl, Br, I, CN, N$_3$) are described.

When a methanolic solution of *N,N*-dimethylhydrazine was added to a solution of the tetrahalogenobenzyl ether (1; R = CH$_2$Ph) in tetrahydrofuran (THF) a white, crystalline product, soluble in water, methanol, and THF but not in diethyl ether was obtained. Elemental analysis and spectral evidence (^{19}F n.m.r.) precluded the possibility that one of the α-fluorine atoms had been substituted by the hydrazine, although this was to be expected by analogy with the behaviour of 3,5-dichlorotrifluoropyridine, its 4-substituted derivatives, and even of the less reactive 4-substituted tetrachloropyridine, towards nucleophiles.[2] Treatment of an aqueous solution of the product with hydrochloric acid or with silver nitrate at room temperature gave an immediate precipitate of 3,5-dichloro-2,6-difluoro-4-hydroxypyridine (1; R = H) (referred to hereafter as haloxydine) or its silver salt. Addition of toluene-*p*-sulphonic acid to a methanolic solution of the product furnished the hydrazinium sulphonate salt (3) and haloxydine. A prolonged period under reflux in various solvents (acetone, dioxane, xylene) produced no rearrangement of the product, nor did the addition of methyl iodide. On the basis of these observations and the water solubility of the product, we assign to it the salt-like structure (4; R^1 = CH$_2$Ph, R^2 = R^3 = Me, R^4 = NH$_2$ X = F). Two alternative structures, namely the σ-complex (5) (Meisenheimer) and the dihydropyridine (6) were also considered. However, the stability, water solubility, and lack of colour of the product are not in keeping with a σ-complex such as (5) and the low resonance (δ 3.22) for the NMe$_2$ group is incompatible with structure (6). The X-ray crystal structure of the tetrachloro compound (4; X = Cl, R^1 = CH$_2$Ph, R^2 = R^3 = Me, R^4 = NH$_2$), a close analogue of the difluoro compound (4; X = F, R's as before) also supported the salt-like nature of the latter.

The reason for the preferential nucleophilic attack on the benzylic methylene rather than for displacement of the 2-(6)-fluorine lies in the increased susceptibility to alkyl-oxygen cleavage due to the combined action of the ring nitrogen and the (+*I*) effect of the four halogens. Thus the pyridine moiety has become the leaving group as a ' phenolate ion '. Analogous dealkylation reactions are well known in the case of nitro-aryl ethers[3] but less so for alkyl heteroaryl ethers. However, pyridinol ethers have been reported to undergo cleavage by treatment with an oxygen nucleophile under forced conditions or as a side reaction. For instance 4-methoxypyridine when made to react with sodium methoxide at elevated temperature (164 °C) gives the pyridin-4-ol anion [(7) ⟶ (8), R = H)]

(1) X = F
(2) X = Cl

(3)

(4)

(5)

(6)

(7)

(8)
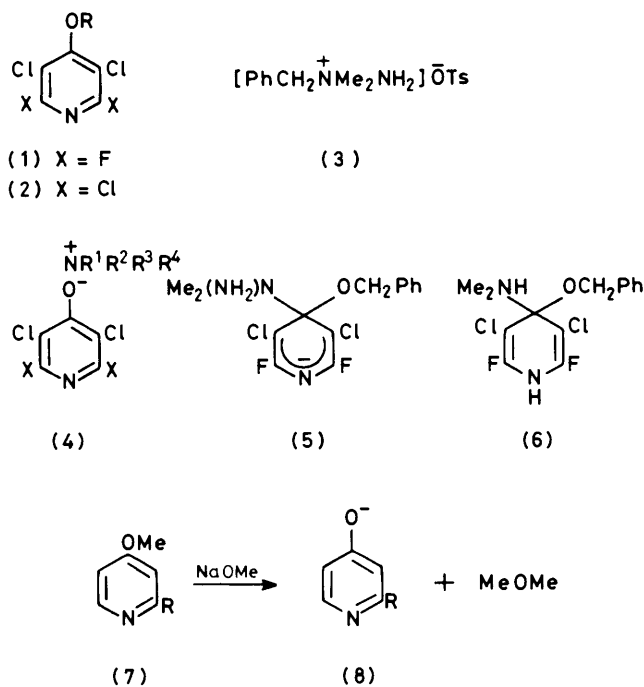
and dimethyl ether,[4] while 2-chloro-4-methoxypyridine (7; R = Cl) yields not only the expected 2,4-dimethoxypyridine but also a little 2-methoxy-4-pyridone when heated with methoxide.[5] Some demethylation as a competing reaction is also observed in the formation of a Meisenheimer adduct from 2-methoxy-3,5-dinitropyridine[6] with sodium methoxide and related reactions, but only with methoxyl, have been cited.[7]
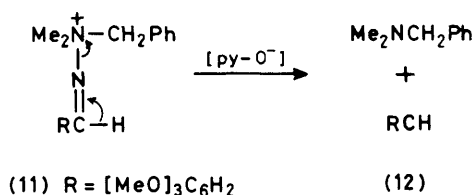
Other nucleophiles reacted with the benzyl ether in an analogous manner; the bidentate *N,N,N',N'*-tetramethyl-ethane-1,2-diamine (TMEDA) gave the ammonium derivative (4; X = F, R^1 = CH$_2$Ph, R^2 = R^3 = Me, R^4 = CH$_2$-CH$_2$NMe$_2$) which was converted with toluene-*p*-sulphonic acid into the double salt (4; R^1, R^2, R^3 as above; R^4 = CH$_2$·CH$_2$NHMe$_2$OTs) and triphenylphosphine gave the phosphonium salt (9). Piperidine, however, displaced one fluorine atom to give the 2-piperidinobenzyl ether (10).

(9)   (10)
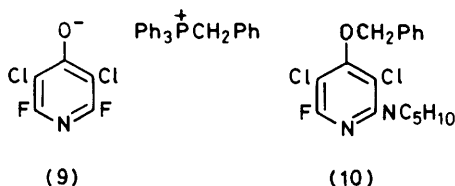
We also carried out similar reactions with the tetrachloro-ether (2; R = CH_2Ph) which gave the corresponding products. For instance, from N,N-dimethylhydrazine we obtained (4; X = Cl, R^1 = NH_2, R^2 = R^3 = Me, R^4 = CH_2Ph), the structure of which was confirmed by an X-ray crystallographic study (see Figure), and which was readily hydrolysed by hydrochloric acid to give tetrachloro-4-hydroxypyridine; TMEDA gave (4; X = Cl, R^1 = CH_2Ph, R^2 = R^3 = Me, R^4 = $CH_2CH_2NMe_2$) and triethylamine (4; R^1 = CH_2Ph, R^2 = R^3 = R^4 = Et) in low yield. Piperidine, contrary to the reaction with the fluoro analogue (1) did not substitute the 2-chlorine atom but yielded the piperidinium salt (4; R^1 = R^2 = H, R^3–R^4 = $[CH_2]_5$) and starting material. The expected N-benzylpiperidinium counterion $C_5H_{10}\overset{+}{N}(CH_2Ph)H$ was probably hydrolysed in the work-up.

4-Tetrachloromethoxypyridine (2; R = Me) behaved similarly to its benzyl analogue yielding the trimethylammonium salt (4; R^1 = R^2 = R^3 = Me, R^4 = $CH_2CH_2NMe_2$) when made to react with TMEDA.

The water solubility of the hydrazinium salt (4; X = Cl or F, R^1 = CH_2Ph, R^2 = R^3 = Me, R^4 = NH_2) and its formal resemblance to the Girard reagents [e.g. Girard T: (Me_3-$\overset{+}{N}CH_2{\cdot}CONHNH_2$) $\overset{-}{C}l$; cf. (4; ($Me_2\overset{+}{N}(CH_2Ph)NH_2OC_5H_4N$)] prompted us to test the feasibility of the former for obtaining water-soluble carbonyl derivatives. However, neither benzaldehyde nor acetophenone could be made to react with the hydrazine (4; X = Cl or F, R^1 = CH_2Ph, R^2 = R^4 = Me, R^4 = NH_2). A prolonged period under reflux of the hydrazine (4; X = F, R^1 = CH_2Ph, R^2 = R^3 = Me, R^4 = NH_2) with 2,4,6-trimethoxybenzaldehyde in dioxan gave 2,4,6-trimethoxybenzonitrile (53.6%), possibly via an usual cleavage of the intermediate hydrazone (11) facilitated by the haloxydine anion and the quaternary leaving group as shown [(11) ⟶ (12)].

$Me_2\overset{+}{N}{-}CH_2Ph$ Me_2NCH_2Ph
    |
    N $\xrightarrow{[py-O^-]}$ +
   ‖
  $RC{-}H$ RCH

(11) R = $[MeO]_3C_6H_2$ (12)

The ready transfer of the benzyl and possibly other alkyl groups from the tetrahalogenopyridine ethers onto nucleophiles could potentially serve as a preparative method for alkyl and aralkyl derivatives. Such a synthesis would be analogous to Mukaiyama's use [8] of 2-halogenopyridinium salts as coupling reagents for the synthesis of carboxylic acid derivatives. Preliminary experiments in which the benzyl ether (2; R = CH_2Ph) was treated with various potassium salts KX (X = Cl, Br, I, N_3, CN) in dimethyl sulphoxide gave reasonable yields (60—80%, not optimised) of the corresponding benzyl derivatives ($PhCH_2X$; X as above). An extension of this study to explore the scope of this reaction is indicated.

The molecular structure of the salt (4; X = Cl, R^1 = CH_2Ph, R^2 = R^3 = Me, R^4 = NH_2) was established by a
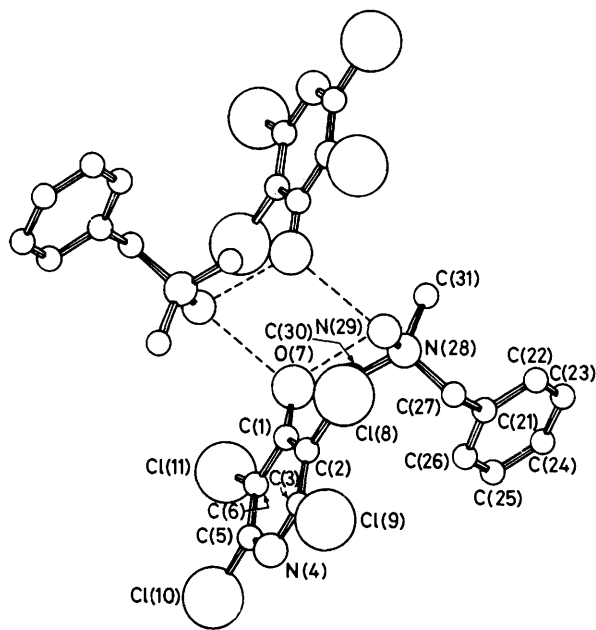

Figure. Hydrogen bonded cluster of two cations and two anions seen down the orthogonal axis Y

single-crystal X-ray study. The Figure shows a hydrogen bonded cluster of two cations and two anions seen down the orthogonal axis Y.

Final atomic co-ordinates and interatomic distances and angles are given in Tables 1 and 2 respectively; these refer to the crystallographic numbering scheme in the Figure. The observed and calculated structure factors together with thermal parameters are available as a Supplementary publication [SUP No. 23710 (11 pp.)].[*]

The structure contains independent cations and anions (Figure). The dimethylbenzylhydrazinium cation has the staggered $trans$-geometry with the torsion angle C(21)−C(27)−N(28)−N(29) = 170.9°; thus the NH_2 group is well removed from the phenyl ring and has the maximum room for hydrogen bonding.

The anion is planar, except for Cl(9) the maximum deviation from the plane defined by the pyridine ring is 0.045 Å [Cl(11)]. Cl(9) lies 0.090 Å from the plane to relieve a close intermolecular contact to Cl(9) of the molecule at $-x$, $1 - y$, $-z$. This contact is only 3.181 Å, as short as the intramolecular Cl(8) $\cdots$ Cl(9) and Cl(10) $\cdots$ Cl(11) distances (3.18 Å average), compared with the sum of van der Waals radii of 3.50 Å. There are no other Cl $\cdots$ Cl contacts in this structure less than 3.7 Å.

Hydrogen bonds connect cations and anions to form dimers in the ac plane centred about $\tfrac{1}{2}$,0,0. Hydrogen bonds are formed by O(7) to both symmetry positions of N(29) of average length 2.909 Å.

Experimental

N.m.r. spectra were recorded at 60 MHz or 90 MHz (^{1}H, ^{19}F) with $SiMe_4$ and CF_3CO_2H respectively as internal standards.

4-Benzyloxy-3,5-dichloro-2,6-difluoropyridine (1; R = CH_2-Ph).—A mixture of the potassium salt of 3,5-dichloro-2,6-difluoro-4-hydroxypyridine (10.0 g, 42.0 mmol), benzyl

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Table 1. Atomic co-ordinates (× 10⁴) for 1-benzyl-1,1-dimethyl-hydrazinium 2,3,5,6-tetrachloropyridin-4-olate

	x/a	y/b	z/c
C(1)	2 353(10)	0 961(10)	9 285(11)
C(2)	2 020(9)	2 090(10)	9 837(10)
C(3)	0 779(9)	2 242(9)	9 325(10)
N(4)	−0 237(7)	1 397(8)	8 317(8)
C(5)	0 065(9)	0 343(10)	7 757(10)
C(6)	1 269(9)	0 053(9)	8 159(10)
O(7)	3 477(6)	0 735(7)	9 720(7)
Cl(8)	3 275(3)	3 271(3)	11 163(3)
Cl(9)	0 404(3)	3 655(3)	10 029(3)
Cl(10)	−1 263(2)	−0 766(3)	6 390(3)
Cl(11)	1 560(3)	−1 352(3)	7 353(3)
C(21)	2 831(8)	−3 245(9)	4 767(10)
C(22)	3 495(11)	6 359(11)	6 333(12)
C(23)	3 122(13)	5 332(13)	6 982(13)
C(24)	2 127(13)	4 295(12)	6 148(15)
C(25)	1 420(13)	4 510(12)	4 631(16)
C(26)	1 780(10)	5 710(11)	3 951(12)
C(27) *	3 236 —	8 080 —	4 047 —
N(28)	4 237(7)	8 195(7)	2 877(8)
N(29)	4 700(8)	9 595(7)	2 493(9)
C(30)	3 635(11)	7 304(11)	1 312(12)
C(31)	5 478(10)	7 861(12)	3 760(13)

* Fixed atom to define origin.

Table 2. Interatomic distances (Å) and selected angles (°) for 1-benzyl-1,1-dimethylhydrazinium 2,3,5,6-tetrachloropyridin-4-olate

C(1)–C(2)	1.415(16)	C(21)–C(22)	1.418(13)
C(2)–C(3)	1.366(14)	C(22)–C(23)	1.368(17)
C(3)–N(4)	1.327(10)	C(23)–C(24)	1.357(15)
N(4)–C(5)	1.327(14)	C(24)–C(25)	1.404(18)
C(5)–C(6)	1.382(14)	C(25)–C(26)	1.372(17)
		C(26)–C(21)	1.385(12)
C(6)–C(1)	1.440(11)	C(21)–C(27)	1.505(9)
C(1)–O(7)	1.271(13)	C(27)–N(28)	1.517(7)
C(2)–Cl(8)	1.736(8)	N(28)–N(29)	1.475(10)
C(3)–Cl(9)	1.750(11)	N(28)–C(30)	1.505(11)
C(5)–Cl(10)	1.755(8)	N(28)–C(31)	1.529(13)
C(6)–Cl(11)	1.729(10)		
C(3)–N(4)–C(5)	113.3(8)	C(22)–C(21)–C(27)	121.0(6)
C(1)–C(2)–Cl(8)	116.4(7)	C(21)–C(27)–N(28)	114.7(5)
C(3)–C(2)–Cl(8)	122.3(8)	C(27)–N(28)–N(29)	108.3(6)
C(2)–C(3)–Cl(9)	120.0(6)	C(27)–N(28)–C(30)	111.7(6)
N(4)–C(3)–Cl(9)	113.6(8)	C(27)–N(28)–C(31)	109.5(6)
C(6)–C(1)–C(2)	112.7(9)		
C(1)–C(2)–C(3)	121.3(8)		
C(2)–C(3)–N(4)	126.4(9)		
Cl(8) · · · Cl(9)	3.167(4)	N(29) · · · O(7)	2.893(20)
Cl(10) · · · Cl(11)	3.194(4)	N(29) · · · O(7)′	2.925(22)
Cl(9) · · · Cl(9)″	3.181(7)		

Symmetry position O(7)′ $(1 - x)$, $-y$, $(1 - z)$
    Cl(9)″ $-x$, $1 - y$, $-z$

bromide (7.2 g, 42.0 mmol) in acetonitrile (100 ml) was stirred at reflux for 29 h. The precipitate (inorganic matter) was filtered off, the filtrate evaporated to dryness, and the residue extracted with hot chloroform. The insoluble residue was unchanged potassium salt (1.47 g, 14.7%). The chloroform solution gave on evaporation the benzyl ether (1; R = CH₂Ph) (7.69 g, 63.1%) recrystallised from methanol, m.p. 79—80 °C (lit.,[9] m.p. 76—78 °C; made from 3,5-dichloro-2,4,6-trifluoropyridine and benzyl alcohol in 45.1% yield), δ_H (CDCl₃) 7.4 (5 H, ArH) and 5.32 (s, 2 H, OCH₂).

4-Benzyloxytetrachloropyridine (2; R = CH₂Ph).—To a mixture of 4-hydroxytetrachloropyridine [10] (10.0 g, 42.9 mmol), potassium carbonate (5.98 g, 43.3 mmol), and a small amount of 18-crown-6-ether (0.5 ml) in acetonitrile (70 ml) kept at reflux was added a solution of benzyl bromide (6.61 g, 38.6 mmol) in acetonitrile (30 ml). The mixture was stirred at reflux for 28 h and worked up as above. Recovered starting material accounted for 1.44 g (12.4%). *4-Benzyloxytetrachloropyridine* (8.19 g, 59.0%) had m.p. 126—127 °C (methanol), δ_H (CDCl₃) 7.42 (5 H, ArH) and 5.21 (s, 2 H, OCH₂) (Found: C, 44.7; H, 2.3; N, 4.4%; M^+, 323. C₁₂H₇Cl₄NO requires C, 44.6; H, 2.2; N, 4.3%; M^+, 323). Without the use of crown ether the yield was 10.8%.

Reactions of 4-Benzyloxy-3,5-dichloro-2,6-difluoropyridine.—(i) *With* N,N-*dimethylhydrazine.* A solution of N,N-dimethylhydrazine (1.04 g, 17.3 mmol) in ethanol (5 ml) was added to a solution of 4-benzyloxy-3,5-dichloro-2,6-difluoropyridine (5.0 g, 17.2 mmol) in tetrahydrofuran (15 ml) and the mixture stirred at room temperature for 6 h. The reaction mixture was poured into diethyl ether to give the N,N-dimethylhydrazinium salt (4; X = F, R¹ = CH₂Ph, R² = R³ = Me, R⁴ = NH₂) (5.1 g, 84.4%) as colourless crystals, m.p. 134—136 °C (melting without decompn.), soluble in water and methanol, insoluble in ether or petroleum δ_H[(CD₃)₂SO], 7.53 (s, 5 H, ArH) 6.04 (s, 2 H, NH₂, exch. with D₂O), 4.65 (s, 2 H, OCH₂), and 3.22 (s, 6 H, Me₂); δ_F (TFA) +3.6 p.p.m. (s, 2F): similar position to the haloxy-

dine anion (Found: C, 48.55; H, 4.5; Cl, 20.5; N, 12.6. C₁₄H₁₅Cl₂F₂N₃O requires C, 48.0; H, 4.3; Cl, 20.25; N, 12.0%).

The salt was stable in boiling acetone, dioxane, or xylene as well as in a tetrahydrofuran solution of methyl iodide at room temperature. Addition of an excess of hydrochloric acid or AgNO₃ to an aqueous solution of the salt gave a quantitative precipitate of haloxydine (3,5-dichloro-2,6-difluoro-4-hydroxypyridine) or its silver salt. Addition of a concentrated methanolic solution of toluene-*p*-sulphonic acid monohydrate to a methanolic solution of the salt gave, on addition of ether, a quantitative precipitate of *benzyldimethylhydrazinium p-tosylate* (3), m.p. 164 °C (Found: C, 59.95; H, 6.5; N, 8.9. C₁₆H₂₂N₂O₃S requires C, 59.6; H, 6.9; N, 8.7%), identical with a sample made from benzyldimethylhydrazinium chloride [11] dissolved in water by addition of silver oxide followed by *p*-TSA.

When a mixture of the hydrazinium salt (4; X = F, R¹ = CH₂Ph, R² = R³ = Me, R⁴ = NH₂) (0.4 g, 1.14 mmol) and benzaldehyde (0.16 g, 1.5 mmol) in water, THF, or dioxan (6 ml) was refluxed for 2—6 h starting materials were recovered quantitatively. Acetophenone gave a similar result. A similar experiment with 2,4,6-trimethoxybenzaldehyde in dioxan or water gave after 10 h under reflux and evaporation of the solvent, a precipitate. Chromatography on silica with chloroform–petroleum (3 : 1) furnished 2,4,6-trimethoxybenzonitrile (53.6%), m.p. 141 °C (lit.,[12] 143—144 °C) identified on the basis of its elemental analysis and i.r. and ¹H n.m.r. spectra. Further elution with ethyl acetate gave a resin which was dissolved in water. Extraction of the aqueous solution with ether after basification with sodium hydrogen carbonate furnished N-benzyl-N,N-dimethylamine as an oil identified on the basis of its elemental analysis and ¹H n.m.r. spectrum.[13]

(ii) *With* N,N,N′,N′-*tetramethylethane-1,2-diamine* (TMEDA). A solution of TMEDA (0.4 g, 3.44 mmol) in methanol (1 ml) was added to a tetrahydrofuran solution (5 ml) of the benzyl ether (1; R = CH₂Ph) and stirred at room

temperature during 18 h. When the mixture was poured into diethyl ether the N-[2-N',N'-*dimethylaminoethylene*]-N-*benzyl*-N,N-*dimethylammonium* salt of haloxydine (4; X = F, R' = CH₂Ph, R² = R³ = Me, R⁴ = CH₂·CH₂NMe₂), m.p. 104—106 °C (1.16 g, 82.9%) was precipitated, δ_H [(CD₃)₂SO], 7.54 (s, 5 H, ArH), 4.62 (s, 2 H), 3.44 (t, 2 H), 3.03 (s, 6 H) 2.74 (t, 2 H), and 2.2 (s, 6 H) (Found: C, 53.1; H, 5.5; N, 10.5. C₁₈H₂₃Cl₂F₂N₃O requires C, 53.2; H, 5.7; N, 10.3%). A mixture of this salt (0.2 g) and *p*-TSA (0.084 g) in THF (5 ml) was stirred for 5 min and then poured into diethyl ether to precipitate the double salt (4; X = F, R¹ = CH₂Ph, R² = R̄³ = Me, R⁴ = [CH₂·CH₂·NHMe₂]OTs) (Found: C, 51.9; H, 5.55; N, 6.9. C₂₅H₃₁Cl₂F₂N₃O₄S requires C, 51.9; H, 5.4; N, 7.3%).

(iii) *With piperidine*. A methanol solution (1 ml) of piperidine (0.29 g, 3.41 mmol) was added to a solution of the benzyl ether (1.0 g, 3.45 mmol) in THF (5 ml). The reaction mixture was stirred during 15 h at room temperature and the solvent was driven off to give a solid which was recrystallised from methanol to yield 4-benzyloxy-3,5-dichloro-2-fluoro-6-piperidinopyridine (10) (0.64 g, 52.4%), m.p. 68 °C, δ_H ([CD₃]₂SO) 7.44br (5 H), 5.2 (s, 2 H), 3.28br (4 H), and 1.6 (s, 6 H) (Found: C, 57.5; H, 4.6; N, 7.6. C₁₇H₁₇Cl₂FN₂O requires C, 57.5; H, 4.8; N, 7.9%). The mother liquor deposited starting material (0.42 g, 42%).

(iv) *With triphenylphosphine*. A mixture of the benzyl ether (1.0 g, 3.45 mmol), triphenylphosphine (0.91 g, 3.47 mmol), and THF (12 ml) was stirred under reflux for 5 h. The solvent was driven off and the residue recrystallised from an ethyl acetate–petroleum (1 : 1) to give the *phosphonium salt* (9), m.p. 125—126 °C (0.6 g, 31.6%), δ_H ([CD₃]₂SO) 7.8br (20 H, ArH) and 5.21 (s, 2 H) (Found: C, 65.3; H, 4.1; N, 2.5. C₃₀H₂₂Cl₂F₂NOP requires C, 65.2; H, 4.0; N, 2.5%).

Reactions of 4-Benzyloxytetrachloropyridine (2; R = CH₂Ph).—(i) *With* N,N-*dimethylhydrazine*. The procedure was as described for the difluoro compound (1; R = CH₂Ph) and gave the N,N-*dimethylhydrazinium salt* (4; X = Cl, R¹ = CH Ph, R² = R³ = Me, R⁴ = NH₂) (74.7%), m.p. 143—145 °C ¹H δ ([CD₃]₂SO), 7.53 (s, 5 H, ArH), 6.1 (s, 2 H, NH₂, exch. with D₂O), 4.67 (s, 2 H, CH₂), and 3.23 (s, 6 H, 2 Me) (Found: C, 43.9; H, 3.9; N, 11.2. C₁₄H₁₅Cl₄N₃O requires C, 43.9; H, 3.95; N, 11.0%). Starting material (29.4%) was recovered from the ethereal solution (*cf.* the difluoro isomer). Addition of an excess of hydrochloric acid to an aqueous solution of the salt gave a quantitative precipitate of tetrachloro-4-hydroxypyridine.

Addition of an excess of benzaldehyde or acetophenone to a hydrazinium salt solution in water, THF, or dioxan caused no reaction even after 20 h under reflux, the salt being recovered quantitatively.

(ii) *With TMEDA*. Under conditions described above for the fluoro analogue (1; R = CH₂Ph), the *diaminotetramethyl salt* (4; X = Cl, R¹ = CH₂Ph, R² = R³ = Me, R⁴ = CH₂-CH₂NMe₂) (74.6%), m.p. 107 °C was obtained, δ_H [(CD₃)₂SO] 7.55 (s, 5 H, ArH), 4.6 (s, 2 H, CH₂), 3.43 (t, 2 H), 3.02 (s, 6 H, Me₂), 2.75 (t, 2 H), and 2.2 (s, 6 H, Me₂) (Found: C, 49.1; H, 5.4; N, 9.6. C₁₈H₂₃Cl₄N₃O requires C, 49.2; H, 5.3; N, 9.6).

(iii) *With piperidine*. A methanolic solution (1.5 ml) of piperidine (0.26 g, 3.05 mmol) was added to the benzyl ether (1 g, 3.10 mmol) in THF (15 ml) and the mixture stirred at room temperature for 16 h. When it was poured into diethyl ether the *piperidinium salt* (4; X = Cl, R¹ = R² = H, R³-R⁴ = ([CH₂]₅) was obtained (0.4 g, 40.8%), m.p. 164 °C (Found: C, 38.0; H, 3.95; N, 9.0. C₁₀H₁₂Cl₄N₂O requires C, 37.8; H, 3.8; N, 8.8%).

(iv) *With triethylamine*. A THF solution (10 ml) of the benzyl ether (2; R = CH₂Ph, 1.0 g, 3.1 mmol) and triethylamine (0.31 g, 3.1 mmol) was heated for 3.5 h under reflux and then poured into diethyl ether to give the *triethylammonium salt* (4; R¹ = R² = R³ = Et, R⁴ = CH₂Ph), p. 93 °C (0.28 g, 21.4%) was precipitated, δ_H ([CD₃]₂SO) 7.5 (s, 5 H, ArH), 4.48 (s, 2 H), 3.17 (q, 6 H), and 1.3 (t, 9 H) (Found: C, 50.9; H, 5.3; N, 6.7. C₁₈H₂₂Cl₄N₂ requires C, 51.0; H, 5.2; N, 6.6%). Evaporation of the solvent deposited unchanged benzyl ether (2; R = CH₂Ph) (78.0%).

Reaction of Tetrachloro-4-methoxypyridine with TMEDA.— The methyl ether [14] (2; R = Me) (1.0 g, 4.05 mmol) and the diamine (0.47 g, 4.04 mmol) dissolved in THF (10 ml) were stirred at room temperature for 20 h. The reaction mixture was poured into diethyl ether to precipitate the N-[2-N',N'-*dimethylaminoethylene*]-N,N,N-*trimethylammonium* salt (4; X = Cl, R¹ = R² = R³ = Me, R⁴ = CH₂CH₂NMe₂) (1.3 g, 88.4%), m.p. 115 °C (Found: C, 39.7; H, 5.0; N, 11.6. C₁₂H₁₉Cl₄N₃O requires C, 39.7; H, 5.3; N, 11.6%).

Reaction of the Benzyl Ether (2; R = CH₂Ph) *with Potassium Halides, Cyanide, and Azide*.—To a solution of the benzyl ether (5.0 g, 15.5 mmol) in DMSO (30 ml) was added the required potassium salt (30 mmol of KX: X = Cl, Br, I, CN, or N₃) and the mixture was stirred on a water-bath for 6 h. Insoluble potassium salt was filtered off and the filtrate subjected to fractional distillation, except in the case of the azide which was extracted with ether followed by chromatography of the ethereal extract on alumina. The yields of the PhCH₂X derivatives were as follows: X = Cl (75.4%), Br (62%), I (59.6%), CN (81.3%), and N (68.4%). Identification of the products was by comparison of their i.r., ¹H n.m.r. spectra, and b.p.s with authentic samples obtained by literature methods.[15]

X-Ray Crystal Structure Determination of 1-Benzyl-1,1-*dimethylhydrazinium 2,3,5,6-Tetrachloropyridin-4-olate* (4; X = Cl, R¹ = CH₂Ph, R² = R³ = Me. R⁴ = NH₂).—*Crystal data*. C₁₄H₁₅Cl₄N₃O, M = 383.06, triclinic. a = 10.55 (2), b = 10.53(2), c = 8.193 (7) Å, α = 9.158 (5), β = 99.12 (6), γ = 106.51 (5)°, U = 859.1 Å³, Z = 2, D_c = 1.48 g cm⁻³, $F(000)$ = 392, space group $P\bar{1}$ (no. 2), CuK_α radiation, μ = 61.07 cm⁻¹. Unit-cell dimensions were obtained from zero level Weissenberg photographs on each axis of the triclinic cell and confirmed by comparison of these and upper level photographs with simulations produced by the local program WEISS. Data were collected as Weissenberg photographs for crystals mounted on [100] (layers 0,7) and [010] (layers 0,7). Intensity measurements were carried out by the Science Research Council Microdensitometer Service, Daresbury Laboratory. 1 535 Planes were observed above background.

All calculations were performed on the Dundee University DEC 10 Computer using the SHELX 76 program system,[16] the molecular geometry program XANADU,[17] and the molecular plotting program PLUTO.[18] Atomic scattering factors were from International Tables.[19] The structure was solved using the direct methods routing TANG, the E-map showing the four chlorine atoms and the remaining non-hydrogen atoms of the cation. Refinement and extension of the structure by full-matrix least-squares and Fourier procedures with anisotropic thermal parameters for the chlorine atoms only gave R 0.11. Absorption corrections followed by anisotropic refinement of the remaining non-hydrogen atoms and the inclusion of hydrogen atoms on calculated positions for the carbon atoms and the location of the hydrazine protons on a difference Fourier map gave convergence at R 0.068 for 106 refined parameters. Unit weights were used

throughout. No features above 0.4 e/Å³ appeared on a final difference map.

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