Heterocyclic Polyfluoro-compounds. Part XXIII.[1] Reaction of Some 2-, 3-, and 4-Substituted Pyridine 1-Oxides, 5-Methylpyrimidine 1-Oxide, and Quinoline 1-Oxide with Perfluoropropene, and of Pyridine 1-Oxide with Perfluoro-(2-methylpent-2-ene): Synthesis of 2-(1,2,2,2-Tetrafluoroethyl)-pyridines or -pyrimidines and their *N*-Oxides and of 2,2,3-Trifluoro-2,3-dihydro-3-trifluoromethylfuro[3,2-*b*]pyridine

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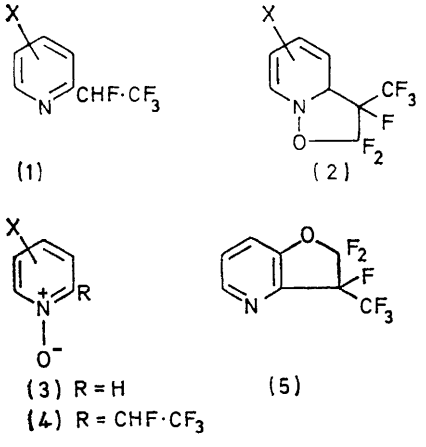
Perfluoropropene reacts thermally with 2-chloro-, 2-cyano-, and 2-(1,2,2,2-tetrafluoroethyl)-pyridine 1-oxide and with 4-methyl-, 4-methoxy-, and 4-nitro-pyridine 1-oxide to yield carbonyl fluoride and the corresponding 2- or 4-substituted 6-(1,2,2,2-tetrafluoroethyl)pyridines. Thermal deoxygenation of 3-bromo-, 3-chloro-, or 3-fluoro-pyridine 1-oxide with perfluoropropene yields a mixture of the corresponding 3- and 5-halogeno-2-(1,2,2,2-tetrafluoroethyl)pyridines plus 2,2,3-trifluoro-2,3-dihydro-3-trifluoromethylfuro[3,2-*b*]pyridine and, in the cases of 3-bromo- and 3-chloro-pyridine 1-oxide, 3- and 5-fluoro-2-(1,2,2,2-tetrafluoroethyl)pyridine. Oxidation of the 2-(1,2,2,2-tetrafluoroethyl)pyridines 2-(CF_3·CHF)C_5H_3NX (X = H, 3-Br, 3-Cl, 3-F, 4-Me, 4-NO_2, 5-Br, 6-Cl, 6-CN, or 6-Me) with peroxy-acid yields the corresponding 1-oxides; 2,2,3-trifluoro-2,3-dihydro-3-trifluoromethylfuro[3,2-*b*]pyridine 4-oxide can be prepared similarly. Deoxygenation of pyridine 1-oxide with perfluoro-(2-methylpent-2-ene) yields 2-(2*H*-hexafluoroisopropyl)pyridine.

Reaction of 5-methylpyrimidine 1-oxide with perfluoropropene yields 5-methyl-4- and 5-methyl-2-(1,2,2,2-tetrafluoroethyl)pyrimidine; oxidation of the former with peroxy-acid gives predominantly 5-methyl-4-(1,2,2,2-tetrafluoroethyl)pyrimidine 1-oxide.

THERMAL reaction of pyridine 1-oxide with perfluoropropene yields 2-(1,2,2,2-tetrafluoroethyl)pyridine (1; X = H),[2-4] a useful plant growth regulator,[3] possibly *via* initial formation of the isoxazolidine (2; X = H).[2] Similarly, 2- and 4-methylpyridine 1-oxides have been converted into the corresponding 6-(1,2,2,2-tetrafluoroethyl) derivatives (1; X = 2- or 4-Me), and the 1-oxides of 3-methylpyridine and pyridine-3-carboxylic acid into mixtures of 2- and 6-(1,2,2,2-tetrafluoroethyl) derivatives (1; X = 3- or 5-Me; X = 3- or 5-CO_2H).[2,3]



Reaction of Monosubstituted Pyridine 1-Oxides with Perfluoropropene.—Liquid-phase thermal reaction between the monosubstituted 1-oxides (3; X = 2-Cl, 2-CN, 2-CHF·CF_3, 4-Me, 4-OMe, or 4-NO_2) and perfluoropropene gave the corresponding tetrafluoroethylpyridines (1) (20—60%) together with carbonyl fluoride and 2*H*-heptafluoropropane. The ' air-sensitive solids ' observed previously[2] proved to be hygroscopic hydrofluorides of the pyridines obtained. Conversion of the pyridines thus prepared, and of 2-(1,2,2,2-tetrafluoroethyl)pyridine, into the corresponding 1-oxides (4; X = H, 2-Cl, 2-CN, 2-CHF·CF_3, 4-Me, or 4-NO_2) was effected with hot aqueous H_2O_2–RCO_2H (R = Me or CF_3).

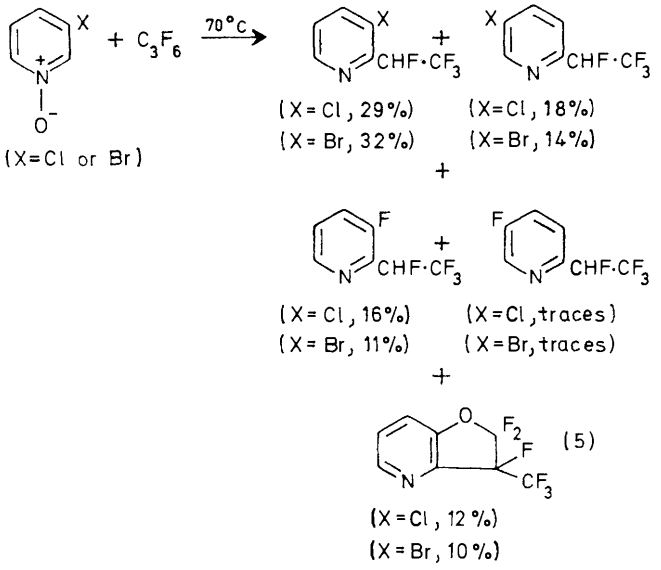
Treatment of 3-fluoropyridine 1-oxide with perfluoropropene at 80 °C gave both 3- and 5-fluoro-2-(1,2,2,2-tetrafluoroethyl)pyridine (33 and 7.5% yield, respectively) together with the novel heterocycle 2,2,3-trifluoro-2,3-dihydro-3-trifluoromethylfuro[3,2-*b*]pyridine (5) (8.5%); the same three products, plus the expected 3- and 5-chloro- (or -bromo-) derivatives of 2-(1,2,2,2-tetrafluoroethyl)pyridine, were formed in an analogous reaction involving 3-chloro- (or -bromo-) pyridine 1-oxide (see Scheme 1).

The structure of the furo[3,2-*b*]pyridine (5) was established through chemical and spectroscopic investigations. That it was not the isomeric pyridocyclobutene *N*-oxide (6), which could plausibly arise *via* electrophilic attack by perfluoropropene at the 2-position of a 3-halogenopyridine 1-oxide, followed by closure of the $-CF_2·\overline{C}F·CF_3$ side-chain on to the 3-position and subsequent loss of hydrogen halide, was clearly indicated by its failure to undergo deoxygenation when heated with phosphorus trichloride, and by its conversion into a crystalline *N*-oxide (7) (70% yield) with hot 30% H_2O_2 (aq.)–$CF_3·CO_2H$.

The ^{1}H n.m.r. spectra of the furo[3,2-*b*]pyridine (5) and its 4-oxide (7) clearly revealed the site of ring fusion, and the ^{19}F spectra were fully consistent with the assigned structure and orientation of the hexafluorinated dihydrofuro moiety (see Supplementary Publication). The

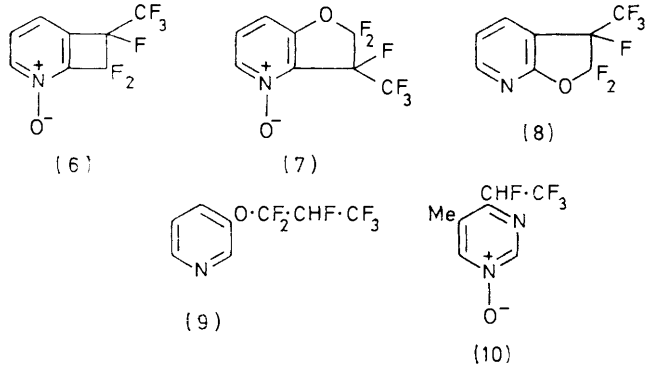
[1] Part XXII, R. E. Banks and T. J. Noakes, *J.C.S. Perkin I*, 1975, 1419.
[2] E. A. Mailey and L. R. Ocone, *J. Org. Chem.*, 1968, **33**, 3343.
[3] E. A. Mailey and L. R. Ocone, U.S.P. 3,534,056/1970.
[4] R. E. Banks, J. M. Birchall, R. N. Haszeldine, and R. Rowland, unpublished work carried out in 1966—1967.

effect of *N*-oxidation on the chemical shifts of the CF_3 (noticeably deshielded) and CF (slightly shielded) fluorines is in keeping with the data obtained for the 2-(CHF·CF_3)-substituted pyridine–pyridine 1-oxide pairs examined so far (see Supplementary Publication); this



SCHEME 1 Yields in parentheses refer to materials isolated

militates against structure (8), formation of which is difficult to envisage from a mechanistic viewpoint;

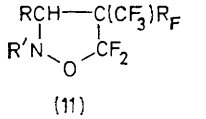


additionally, structure (5) for the dihydrofuropyridine is supported by the relationship between the ^1H chemical shift data and those for 3-(2*H*-hexafluoropropoxy)pyridine (9), prepared by treatment of 3-hydroxypyridine with perfluoropropene in the presence of potassium carbonate.[5]

Extensions of the Fluoroalkylation Procedure.—Both quinoline 1-oxide and 5-methylpyrimidine 1-oxide underwent reductive α-fluoroalkylation when heated with perfluoropropene: at 70 °C the former heterocycle gave a mixture of 2-(1,2,2,2-tetrafluoroethyl)quinoline and its hydrofluoride in 22% total yield, and the latter gave a *ca.* 3 : 1 mixture (36%) of 5-methyl-4- and -2-(1,2,2,2-tetrafluoroethyl)pyrimidine. Treatment of 5-methyl-4-(1,2,2,2-tetrafluoroethyl)pyrimidine with 30% H_2O_2 (aq.)–$MeCO_2H$ at 70 °C gave a low yield (15%) of a crystalline oxide, believed to be the 1-oxide (10), together with traces of a yellow oil that appeared from mass spectral data to contain the other isomer (*i.e.* the 3-oxide). Structure (10), which is that expected for the major product on consideration of inductive and steric effects in the parent pyrimidine, is consistent with the ^{19}F n.m.r. chemical shift data observed, since *N*-oxidation of the 2-(1,2,2,2-tetrafluoroethyl)pyridines prepared in this work causes deshielding of the CF_3 group and shielding of the CF group (see Supplementary Publication).

Regarding changes in the structure of the electrophilic component of the perfluoropropene–pyridine 1-oxide reactant pair, perfluoro-(2-methylpent-2-ene) gives 2-(2*H*-hexafluoroisopropyl)pyridine (15%) and perfluoropropionyl fluoride, as expected on the basis of the mechanistic sequence proposed previously.[2]

Mechanism.—Perfluoropropene is an electrophilic olefin, well known to undergo nucleophilic attack at the terminal sp^2 carbon atom by a range of nucleophiles under relatively mild conditions.[6] Thus the original proposal [2] that the first stage in the reaction between pyridine 1-oxide and this olefin involves stepwise formation of an isoxazolidine [(2; X = H)] is not unreasonable; the alternative is ' concerted ' attachment of perfluoropropene to the 1,3-dipolar system provided by the 1-oxide. Attempts to isolate or detect the formation of an isoxazolidine (2; X = 3- or 5-Br) from perfluoropropene and 3-bromopyridine 1-oxide (this system was chosen because the oxide is a liquid at room temperature) proved abortive, although isolable isoxazolidines (11) are said to be formed from perfluoropropene or perfluoroisobutene and acyclic nitrones at room temperature.[7] However, deoxygenation coupled with ring 2-substitution when a heteroaromatic *N*-oxide is treated with an electrophilic dipolarophile is well established and initial formation of a labile non-aromatic cycloadduct is normally assumed; [2,8] such is the case here, and a possible mode of decomposition of an isoxazolidine derived from perfluoropropene and a 3-halogenopyridine 1-oxide is shown in Scheme 2. Release of the oxyanion (12) in



(11)

R_F = F or CF_3; R = Me or Ph;

R' = Et or $PhCH_2$

[5] Belg. P. 793,726/1973.

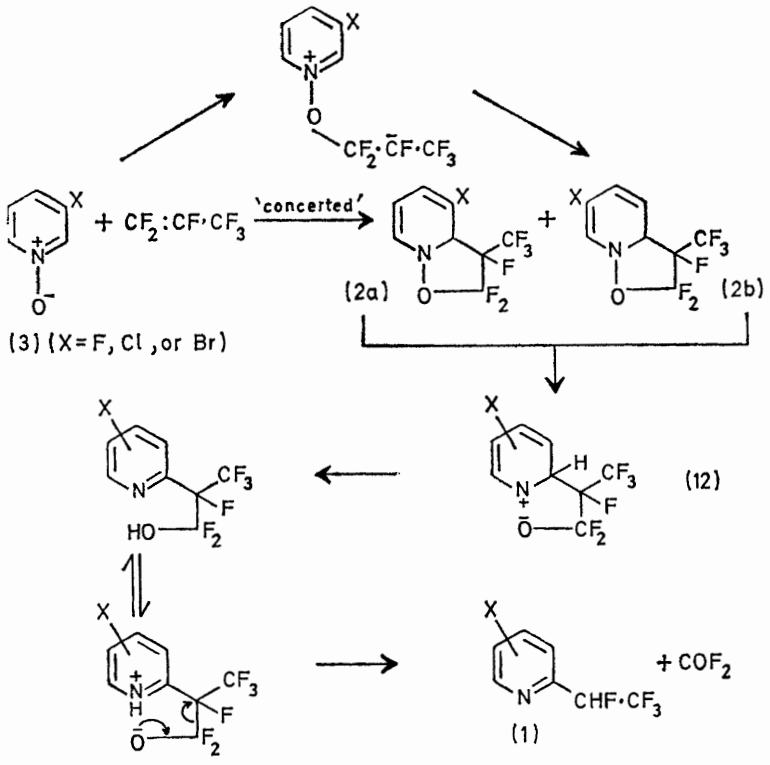
[6] R. E. Banks, ' Fluorocarbons and their Derivatives,' 2nd edn., Macdonald, London, 1970.

[7] I. L. Knunyants, E. G. Bykhovskaya, V. N. Frosin, I. V. Galakhov, and L. I. Regulin, *Zhur. Vsesoyuz. Khim. obshch. im. D.T. Mendeleeva*, 1972, **17**, 356.

[8] See, for example, R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565; R. Huisgen, H. Seidl, and J. Wulff, *Chem. Ber.*, 1969, **102**, 915; R. A. Abramovitch and I. Shinkai, *J.C.S. Chem. Comm.*, 1973, 569.

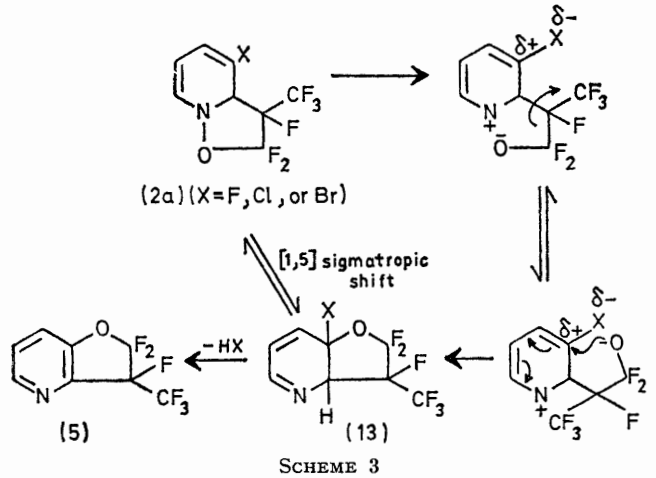
the case of isomer (2a) accounts for formation of 2,2,2-trifluoro-2,3-dihydro-3-trifluoromethylfuro[3,2-*b*]pyridine (5) (see Scheme 3). If homolytic cleavage of an isoxazolidine N–O bond were important, the formation of furopyridines would have been expected in other cases, failure to detect furopyridines in products from reactions involving pyridine 1-oxide or 2- and 4-substituted pyridine 1-oxides argues against this.

In the reactions between 3-chloro- and 3-bromopyridine 1-oxide and perfluoropropene (see Scheme 1),



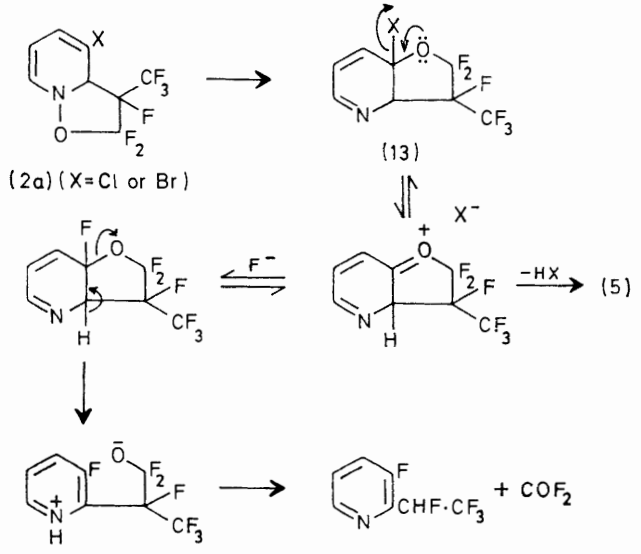
SCHEME 2

particularly the reaction between perfluoropropene and 4-nitropyridine 1-oxide; careful search (g.l.c., t.l.c.) of



SCHEME 3

the product from perfluoropropene and pyridine 1-oxide for (5) or its immediate precursor [the equivalent of (13)] proved unsuccessful. It is conceivable that the tetrahydrofuropyridine (13) arises *via* symmetry-allowed suprafacial [1,5]- sigmatropic rearrangement of (2a); the possibility of fluorine-for-bromine (or -chlorine) exchange occurring *via* fluoride-ion attack on either the parent 3-halogenopyridine 1-oxide or the bromo- (or chloro-) 2-(1,2,2,2-tetrafluoroethyl)pyridines formed was



SCHEME 4

eliminated by heating the bromo-compounds separately with caesium fluoride in acetonitrile or tetramethylene sulphone at 80—110 °C for 2—4 days: the starting materials were recovered almost quantitatively. Additionally, 2,2,3-trifluoro-2,3-dihydro-3-trifluoromethylfuro[3,2-*b*]pyridine was recovered in 84% yield after treatment with caesium fluoride in tetramethylene sulphone at 110—135 °C for 4 days, and no 3-fluoro-2-(1,2,2,2-tetrafluoroethyl)pyridine appeared to be formed. Of several mechanisms that can be written to account for the halogen-exchange observed, the one presented in Scheme 4 is preferred.[9]

EXPERIMENTAL

Spectroscopic and analytical data are available as Supplementary Publication No. SUP 21727 (20 pp., 1 microfiche).†

Reactions between Pyridine 1-Oxides and Perfluoropropene.—These were carried out in the absence of air in stainless steel rocking autoclaves under conditions (70—80 °C, 35—65 atm. initial pressure) where liquid olefin (P_c *ca.* 30 atm., T_c *ca.* 85 °C) was present. In each case, the volatile product comprised perfluoropropene, carbonyl fluoride, and 2*H*-heptafluoropropane; the involatile product (which was always a dark brown liquid) was worked up either by subjecting it to vacuum distillation followed, if necessary, by chromatographic purification of distillates (method A) or by pouring it directly from the autoclave into vigorously stirred water then carrying out an extraction with methylene chloride prior to distillation, *etc.* (method B, as exemplified below). The details are listed in Table 1.

Reaction of Pyridine 1-Oxide with Perfluoro-(2-methylpent-2-ene).—Pyridine 1-oxide (10.0 g, 105 mmol) was heated with perfluoro-(2-methylpent-2-ene) (19.4 g, 64.7 mmol) at 70 °C for 72 h in a stainless steel rocking autoclave (100 cm³). Examination of the gaseous product by i.r. spectroscopy showed it to contain perfluoropropionyl fluoride, 2*H*-2-(trifluoromethyl)decafluoropentane, and perfluoro-(2-methylpent-2-ene). The involatile product, a dark brown liquid, was poured from the autoclave's cup into vigorously stirred water (50 cm³); the aqueous mixture was extracted with methylene chloride (3 × 50 cm³) and the extract was evaporated; the dark brown residue was heated slowly from 20 to 180 °C at *ca.* 0.1 mmHg pressure in a simple short-path distillation apparatus with a receiver cooled to −78 °C, and the pale-yellow two-component (by t.l.c.) distillate (7.5 g) was separated by column chromatography (silica gel; chloroform) into pyridine (2.0 g, 25.3 mmol, 39%) and 2-(2H-*hexafluoroisopropyl)pyridine* (2.2 g, 9.6 mmol, 15%) (Found: C, 41.9, 41.6; H, 1.7, 2.1; F, 49.5; N, 6.2%; $M^{+\cdot}$, 229. $C_8H_5F_6N$ requires C, 41.9; H, 2.2; F, 49.8; N, 6.1%; *M*, 229), as plates, m.p. 35 °C, b.p. (Siwoloboff) 144—145 °C at 758 mmHg.

Preparation of Substituted 2-(1,2,2,2-Tetrafluoroethyl)pyridine 1-Oxides.—The details are listed in Table 2. Typically, aqueous hydrogen peroxide (30%; 6.0 cm³) was added to a solution of 2,6-bis-(1,2,2,2-tetrafluoroethyl)pyridine (3.00 g, 10.75 mmol) in trifluoroacetic acid (20 cm³). The stirred mixture was heated at 80 °C for 7 h, then more 30%

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

[9] J. M. Robinson, Ph.D. Thesis, University of Manchester, 1974.

TABLE 1

Reactions between pyridine 1-oxides (3) and perfluoropropene

1-Oxide (3) (g, mmol)	C_3F_6 (g, mmol)	Temp., time (°C, h)	Products * (g, mmol % yield)
X = H (5.0, 53)	20.9, 139	70, 24 [a]	(1; X = H) [b,c] (3.0, 16.8, 32)
X = 2-CHF·CF_3 (39.0, 200)	36.0, 240	78, 72 [a]	(1; X = 6-CHF·CF_3) [b,d] (13.0, 46.6, 23)
X = 2-Cl (14.7, 114)	36.0, 240	70, 66 [a]	(1; X = 6-Cl) [b,e] (8.0, 37.5, 33)
X = 2-CN (25.0, 209)	120, 800	75, 72 [f,g]	(1; X = 6-CN) [b,h] (24.0, 118, 57)
X = 4-Me (10.0, 91.7)	115, 766	70, 48 [f,g]	(1; X = 4-Me) [b,i] (6.0, 31, 34) (14) [b,j] (0.2, 0.9, 1)
X = 4-OMe (21.0, 168)	101, 673	70, 60 [f]	(3; X = 4-OMe) [k,l] (6.3, 30.1, 18)
X = 4-NO_2 (10.0, 70.9)	115, 766	70, 48 [f,g]	(1; X = 4-NO_2) [b,m] (4.8, 21.4, 30) [n]
X = 3-Br (56.0, 322)	101, 673	70, 48 [f,o]	(1; X = 3-F) [p] (7.0, 36, 11) (5) [q] (8.0, 33, 10) (1; X = 5-Br) [r] (12.0, 46.5, 14) (1; X = 3-Br) [s] (27.0, 104, 32)
X = 3-Cl (25.0, 193)	30.0, 200	70, 48 [a,t]	(1; X = 3-F) [u] (6.0, 30.5, 16) (1; X = 5-Cl) [v] (7.4, 34.7, 18) (5) [u] (5.7, 23.5, 12) (1; X = 3-Cl) [w] (12.1, 56.7, 29)
X = 3-F (17.0, 150)	31.5, 210	80, 48 [a,z]	(1; X = 5-F) [y] (2.2, 11.2; 7.5) (1; X = 3-F) [u] (9.8, 49.7, 33) (5) [u] (3.1, 12.8, 8.5)

* For analytical data see Supplementary Publication.

[a] 100 cm³ Autoclave. [b] Worked up by method A. [c] B.p. 141—142 °C at 760 mmHg (lit.,[2] 142 °C at 'ambient pressures'). [d] B.p. (Siwoloboff) 165 °C at 760 mmHg. [e] B.p. (Siwoloboff) 178 °C at 761 mmHg. [f] 500 cm³ Autoclave. [g] Acetonitrile (50 cm³) used as solvent. [h] B.p. 70—72 °C at 1 mmHg. [i] B.p. 58—60 °C at 11 mmHg [lit.,[2] 166 °C at 760 mmHg (presumably)]. [j] 4-Methyl-2-(1,2,2,2-tetrafluoroethyl)pyridinium fluoride, m.p. 102 °C (from acetone), identified spectroscopically. [k] Worked up by method B. [l] Isolated finally as a liquid by column chromatography [silica gel eluted with light petroleum (b.p. 60—80 °C)–chloroform (80 : 20 v/v)]. [m] B.p. 98—100 °C at 11 mmHg. [n] At 70 °C for 72 h, the yield was 38%. [o] Product worked up by method B, material isolated by vacuum distillation (b.p. 100 °C at *ca.* 0.2 mmHg) being subjected to preparative g.l.c. (6 m Kel-F 90 on Celite at 150 °C); the compounds isolated are listed in order of increasing g.l.c. retention times, but the first compound to be eluted (estimated yield 0.3%) was (1; X = 5-F). [p] B.p. (Siwoloboff) 162 °C at 760 mmHg. [q] B.p. (Siwoloboff) 178 °C at 760 mmHg. [r] B.p. (Siwoloboff) 184 °C at 760 mmHg. [s] B.p. (Siwoloboff) 207 °C at 760 mmHg. [t] Product worked up by method B, and material boiling in the range 20—80 °C at 0.2 mmHg then subjected to preparative g.l.c. (3.5 m TXP on Celite at 125 °C) to give the compounds listed (in order of increasing retention time); traces of (1; X = 5-F) were also present but were not collected. [u] Identified spectroscopically (i.r., n.m.r., and mass). [v] B.p. (Siwoloboff) 162 °C at 760 mmHg. [w] B.p. (Siwoloboff) 202 °C at 760 mmHg. [z] Product worked up by method B, material isolated by vacuum distillation (b.p. 25—100 °C at *ca.* 0.2 mmHg) being subjected to preparative g.l.c. (6 m Kel-F 90 on Celite at 130 °C). [y] B.p. 148 °C at 760 mmHg.

hydrogen peroxide solution (2 cm³) was added and the temperature was kept at 80 °C for a further 15 h. The product was evaporated at reduced pressure (0.2 mmHg; pot temperature 20—30 °C) and the residue (*ca.* 10 cm³) was neutralised (Na_2CO_3) then extracted with chloroform (3 × 10 cm³). The extract was dried ($MgSO_4$) and distilled, giving 2,6-*bis*-(1,2,2,2-*tetrafluoroethyl*)*pyridine* 1-*oxide* (1.90 g, 6.7 mmol, 62%) (Found: C, 36.3; H, 1.9; F, 51.4; N, 4.5%; $M^{+\cdot}$, 295. $C_9H_5F_8NO$ requires C, 36.6; H, 1.8; F, 51.5; N, 4.7%; *M*, 295), b.p. 44—45 °C at 1 mmHg.

TABLE 2

Preparation of substituted 2-(1,2,2,2-tetrafluoroethyl)-pyridine 1-oxides (4)

			1-Oxide *		
X [a]	Peroxy-acid system [b]	Conditions (°C, h)	Yield (%)	M.p. (°C)	B.p. (°C, mmHg)
H	A	90, 18	84	74 [c]	
2-Cl	A	80, 27	65	54—56 [d]	
2-CN	B	80, 72	47	79—81 [e]	
4-Me	A	90, 18	77	81—83 [f]	
4-NO_2	C	80, 19	56		81—82, 0.2
3-Br	A	90, 23	39		69—71, 0.1
3-Cl	C	80, 24	83	55—56 [g]	55—57, 0.2
3-F	C	80, 22	74	69 [h]	
5-Br	C	90, 18	67		*i*

* For analytical data see Supplementary Publication.

[a] For X = CHF·CF_3, see text. [b] A = 30% H_2O_2 (aq.)–glacial AcOH; B = 40% H_2O_2 (aq.)–glacial AcOH; C = 30% H_2O_2 (aq.)–CF_3·CO_2H. [c] White prisms from $CHCl_3$. [d] Pale yellow plates, purified by column chromatography (silica gel eluted with $CHCl_3$). [e] Plates from $CHCl_3$. [f] Prisms from $CHCl_3$. [g] White crystals from $CHCl_3$. [h] Prisms from Me_2CO. [i] Pale yellow oil isolated by column chromatography (silica gel eluted with $CHCl_3$).

Reactions of 2,2,3-*Trifluoro*-2,3-*dihydro*-3-*trifluoromethylfuro*[3,2-b]*pyridine*.—(a) *Oxidation*. A mixture of the furopyridine (0.60 g, 2.47 mmol), trifluoroacetic acid (5 cm³), and aqueous hydrogen peroxide (30%; 1.5 cm³) was heated under reflux at 80 °C for 7 h; more aqueous hydrogen peroxide (2 cm³) was then added and heating continued for a further 7 h. The product (at 20—30 °C) was evaporated under reduced pressure (0.2 mmHg), and the residue was neutralised (Na_2CO_3) then extracted with chloroform (3 × 10 cm³); the extract was dried ($MgSO_4$) and evaporated, and the crude pale yellow residue was recrystallised from chloroform to provide white plates of 2,2,3-*trifluoro*-2,3-*dihydro*-3-*trifluoromethylfuro*[3,2-b]*pyridine* 4-*oxide* (7) (0.45 g, 1.74 mmol, 70%) (Found: C, 37.1; H, 1.2; F, 42.7; N, 4.9%; $M^{+\cdot}$, 259. $C_8H_3F_6NO_2$ requires C, 37.1; H, 1.2; F, 44.0; N, 5.4%; *M*, 259), m.p. 65—66 °C.

(b) *Deoxygenation*. A homogeneous mixture of phosphorus trichloride (0.6 cm³), chloroform (5 cm³), and 2,2,3-trifluoro-2,3-dihydro-3-trifluoromethylfuro[3,2-*b*]pyridine (0.6 g), prepared at 0 °C, was warmed to room temperature then heated under reflux on a steam-bath for 1 h. The product was allowed to cool to 21 °C then poured on to crushed ice (*ca.* 10 g); the aqueous mixture was neutralised (aq. 30% KOH) and extracted with chloroform (3 × 10 cm³). Evaporation of the extract afforded the furopyridine starting material (0.6 g, 100%), identified by i.r. spectroscopy and t.l.c.

5-*Methyl*-2- *and* -5-*Methyl*-4-(1,2,2,2-*tetrafluoroethyl*)*pyrimidine*.—5-Methylpyrimidine 1-oxide (26.0 g, 0.236 mol; prepared [10] from commercial 5-methylpyrimidine) and hexafluoropropene (115 g, 0.767 mol) were heated together in the absence of air in a stainless steel rocking autoclave (500 cm³) at 75 °C for 24 h. After removal of the gaseous product (shown by i.r. spectroscopy to be a mixture of hexafluoropropene, carbonyl fluoride, and 2*H*-heptafluoropropane), the involatile product, a dark brown liquid, was poured into vigorously stirred water (50 cm³). The heavy oil that separated was extracted with methylene chloride (3 × 50 cm³); evaporation of the extract followed by short-path vacuum distillation of the residue provided a pale-yellow oil (17.0 g), which collected in the solid CO_2-cooled receiver when the still-pot temperature reached 200 °C at a pressure of *ca.* 0.4 mmHg. Subjection of a sample of the distillate (4.1 g) to preparative g.l.c. (3.5 m TXP column at 150 °C; Perkin-Elmer F21 instrument) gave 5-*methyl*-4-(1,2,2,2-*tetrafluoroethyl*)*pyrimidine* (3.0 g, 15.5 mmol, 27%) (Found: C, 43.0; H, 3.1; F, 38.8; N, 14.2%; $M^{+\cdot}$, 194. $C_7H_6F_4N_2$ requires C, 43.3; H, 3.1; F, 39.2; N, 14.4%; *M*, 194), b.p. 168 °C at 758 mmHg, and 5-*methyl*-2-(1,2,2,2-*tetrafluoroethyl*)*pyrimidine* (1.0 g, 5.15 mmol, 9%) (Found: C, 43.3; H, 3.2; F, 38.8; N, 14.1%; $M^{+\cdot}$, 194), m.p. 34 °C.

N-*Oxidation of* 5-*Methyl*-4-(1,2,2,2-*tetrafluoroethyl*)*pyrimidine*.—Aqueous hydrogen peroxide (30%; 10 cm³) and the pyrimidine (2.0 g, 10.3 mmol) in glacial acetic acid (25 cm³) were heated at 70 °C for 5 h; more hydrogen peroxide (5 cm³) was then added to the mixture, which was kept at 70 °C for a further 20 h. The final product was evaporated at 12 mmHg and the residue (*ca.* 15 cm³) was neutralised (solid Na_2CO_3) and extracted with chloroform (3 × 20 cm³); the extract was dried ($MgSO_4$), then distilled, and the brown still-pot residue was subjected to column chromatography (silica gel; chloroform) to yield 5-methyl-4-(1,2,2,2-tetrafluoroethyl)pyrimidine (0.1 g, 5% recovery), 5-*methyl*-4-(1,2,2,2-*tetrafluoroethyl*)*pyrimidine* 1-*oxide* (0.3 g, 1.43 mmol, 14.6% based on starting material consumed) (Found: C, 40.3; H, 3.2%; $M^{+\cdot}$, 210. $C_7H_6F_4N_2O$ requires C, 40.0; H, 2.9%; *M*, 210), m.p. 111 °C (plates), and a yellow oil believed to contain 5-methyl-6-(1,2,2,2-tetrafluoroethyl)-pyrimidine 1-oxide (0.1 g) (Found: $M^{+\cdot}$, 210. Calc. for $C_7H_6F_4N_2O$: *M*, 210).

2-(1,2,2,2-*Tetrafluoroethyl*)*quinoline*.—A mixture of quinoline 1-oxide (38.0 g, 262 mmol) and perfluoropropene (81 g, 0.54 mol) was heated in a stainless steel rocking autoclave (500 cm³) at 70 °C for 24 h. Removal of the gaseous product (shown by i.r. spectroscopy to be C_3F_6 contaminated with COF_2 and CF_3·CHF·CF_3) followed by short-path distillation of the involatile product, a dark brown oil, gave (at 130 °C and 0.3 mmHg) a mixture (18.0 g) of a pale yellow liquid and a white solid, which was separated by extraction with chloroform into 2-(1,2,2,2-*tetrafluoroethyl*)*quinoline* (4.0 g, 17.5 mmol, 7%) (Found: C, 57.8; H, 3.3; F, 33.0; N, 5.9%; $M^{+\cdot}$, 229. $C_{11}H_7F_4N$ requires C, 57.6; H, 3.1; F, 33.1; N, 6.1%; *M*, 229), m.p. 34 °C (from $CHCl_3$), and 2-(1,2,2,2-*tetrafluoroethyl*)*quinolinium fluoride* (10.0 g, 40.0 mmol, 15%) (Found: C, 53.0; H, 3.4; F, 38.1; N, 5.5. $C_{11}H_8F_5N$ requires C, 53.0; H, 3.2; F, 38.2; N, 5.6%), m.p. 74 °C, a sample of which (5.0 g, 20 mmol) gave 2-(1,2,2,2-tetrafluoroethyl)quinoline [4.3 g, 18.8 mmol, 94% after extraction with light petroleum (b.p. 60—80 °C)] on treatment with an excess of 2M-sodium hydroxide.

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[10] R. H. Wiley and S. C. Slaymaker, *J. Amer. Chem. Soc.*, 1957, **79**, 2233.