Reactions Involving Fluoride Ion. Part VI.[1] Reactions of Tetrafluoroethylene with Pentafluoropyridine and Tetrafluoropyridazine

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Fluoride ion-induced reaction of tetrafluoroethylene with pentafluoropyridine gave perfluoro-4-ethyl, -2,4-diethyl-, and -2,4,5-triethyl-pyridines. The trisubstituted product could not be rearranged, in the presence of fluoride ion at elevated temperatures, to the -2,4,6-isomer. Related studies with perfluoroethylisopropylpyridines indicated that ease of rearrangement of -2,4,5- to -2,4,6-isomers is limited by the stability of the migrating anion. Reaction of tetrafluoroethylene with tetrafluoropyridazine gave perfluoro-4-ethyl-, -4,5-diethyl-, and -3,4,5-triethyl-pyridazines, in low yields, as well as high molecular weight oils. The formation of these oils is attributed to an electron-transfer process.

THE fluoride ion-induced polyfluoroalkylation of pentafluoropyridine with tetrafluoroethylene, to give pentafluoroethyl derivatives, was reported in Part I,[2] and has been described in more detail by Fielding.[3] In reactions under pressure, complex mixtures of products were obtained from which it was difficult to isolate individual components, particularly the mono-, bis-, and tris-pentafluoroethyl isomers. We have now developed atmospheric pressure techniques[4] and find that the degree of substitution is much easier to control; these particular isomers have now been fully characterised.

In the very simple apparatus, the caesium fluoride and solvent are contained in a flask carrying a condenser with an attached bladder. The system is initially evacuated and then filled with tetrafluoroethylene, after which the progress of the reaction may be assessed by observing the collapse of the bladder. In contrast to previous work with hexafluoropropene, where we found that tetrahydro-thiophen dioxide was a very effective solvent,[2,4] with tetrafluoroethylene 2,5,8,11,14-pentaoxapentadecane was more efficient; this corresponds with the results of Graham[5] who used the pentaether in the oligomerisation of tetrafluoroethylene.

A temperature of ca. 80° was necessary for the reaction to proceed at a reasonable rate; this is almost certainly a limitation imposed by the equilibrium constant for the

formation of the perfluoroethyl anion (i) rather than the activation energy for the substitution step (ii). This

$$F^- + CF_2 =\!\!=\!\!= CF_2 \rightleftharpoons CF_3 \cdot CF_2^- \qquad \text{(i)}$$

$$cf. \quad F^- + CF_2 =\!\!=\!\!= CF \cdot CF_3 \rightleftharpoons (CF_3)_2 CF^- \qquad \text{(iii)}$$

follows from the observation that an analogous reaction with perfluoroisopropyl anions, from hexafluoropropene, proceeds more rapidly at 80° than with the tetrafluoroethylene system.[4] Also, polyfluoroalkylation of the more reactive tetrafluoropyridazine with hexafluoropropene proceeds at a reasonable rate at 20°,[6] whereas reaction with tetrafluoroethylene is very slow at this temperature. It is now well established[7,8] that a fluorine atom directly attached to a carbanion centre is considerably less stabilising than a trifluoromethyl group in the same position, i.e. $\bar{C}$–X (X = F or CF_3). Therefore the perfluoroisopropyl anion will be more stable than the pentafluoroethyl anion and correspondingly less

[1] Part V, R. D. Chambers, R. P. Corbally, W. K. R. Musgrave, J. A. Jackson, and R. S. Mathews, *J.C.S. Perkin I*, 1972, 1286.

[2] R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, *J. Chem. Soc. (C)*, 1968, 2221.

[3] H. C. Fielding, B.P. 1,133,492/1968.

[4] R. D. Chambers, R. P. Corbally, and W. K. R. Musgrave, *J.C.S. Perkin I*, 1972, 1281.

[5] D. P. Graham, *J. Org. Chem.*, 1966, **31**, 955.

[6] R. D. Chambers, Yu. A. Cheburkov, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1971, 532.

[7] S. Andreades, *J. Amer. Chem. Soc.*, 1964, **86**, 2003.

[8] J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *J. Amer. Chem. Soc.*, 1961, **83**, 1219.

reactive, but the concentration of anions in (iii) should be greater than in (i) at a particular temperature, thus accounting for the greater rate of substitution with hexafluoropropene. The variation in product distribution, in the case of tetrafluoroethylene, with reaction time is

already been established that attack by $(CF_3)_2CF^-$ at the 5-position in (VII) is kinetically preferred, giving (VIII), but in this case 6-attack giving (IX) is also observed.[4] Thus kinetic control of substitution in (III) by $CF_3 \cdot CF_2^-$ is clear-cut.[11] In a comparative reaction of (III) with

TABLE 1

Fluoride ion-initiated reaction between pentafluoropyridine and tetrafluoroethylene *

Products and yields (%) †

Reaction time (h)	$C_5F_4N(C_2F_5)$ (II)	$C_5F_3N(C_2F_5)_2$ (III)	$C_5F_2N(C_2F_5)_3$ (IV)	$C_5FN(C_2F_5)_4$ (V)	$C_5N(C_2F_5)_5$ (VI)	Conversion (%)
1	76					16
2	49	13	4			53
3	46	17	10			62
4	41	18	10			63
5	38	19	12	1·5		68
6	37	15	13	3		72
7	36	16	30	3	5	76
8	27	20	32	6·5	5·5	79

* At ca. 80° and atmospheric pressure. † Based on the weight of C_5F_5N (I) consumed.

shown in Table 1: under atmospheric pressure conditions the main products are now the mono-, bis-, and tris-pentafluoroethyl derivatives, i.e. those products which we had most difficulty in isolating previously.[2]

(III)

+

(IV)
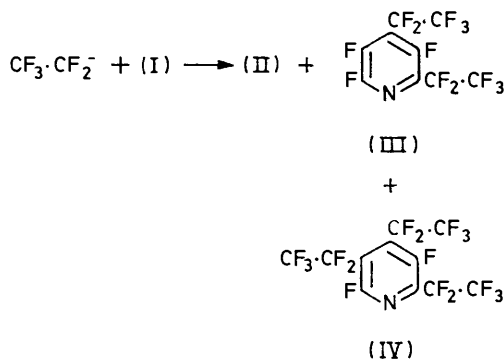
The structures of compounds (II)—(IV) were established by [19]F n.m.r. spectroscopy (see later) and the formation of (II) and (III) is entirely consistent with the many other nucleophilic aromatic substitutions in pentafluoropyridine which have been observed.[2,9,10] In con-

(VII)   (VIII)   (IX)

$R_F = CF(CF_3)_2$

(VII) $\xrightarrow[160°]{F^-}$ (IX) + other products
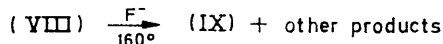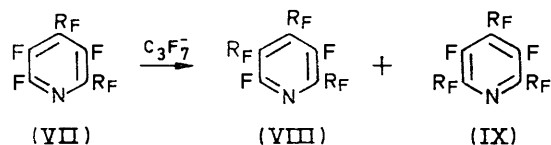
trast, however, the formation of (IV) as the exclusive trispentafluoroethyl derivative is exceptional. It has

$(CF_3)_2 \cdot CF^-$, again 5-attack occurred, giving (X) exclusively. In the formation of these perfluoro(trialkyl-

(III) $\xrightarrow[[CH_2]_4SO_2]{C_3F_6, 80°}$

(X)
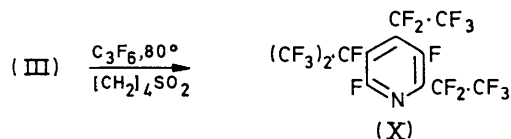
pyridines) the perfluoroalkyl groups in the 2- and 4-positions control the entry of the third group, i.e. a transition-state similar to (XI) is preferred to one which is similar to (XII).[4] Methoxide attack on (III) and (VII) occurs in a similar manner giving exclusively 5-substitution, i.e. with a transition state corresponding to (XI).

Perfluoro-(2,4,5-triethylpyridine) (IV) was heated with caesium fluoride to 160° [conditions under which (VIII) is rearranged[4]] but was unchanged (85% recovery).

(XI)   (XII)

$R_F = CF_2 \cdot CF_3$ or $CF(CF_3)_2$. Nu = $CF_2 \cdot CF_3$, $CF(CF_3)_2$, or OMe

Also, an analogous experiment, but in the presence of perfluoroquinoline which would trap any pentafluoroethyl anions, led to 75% recovery of (IV). This shows that displacement of $CF_3 \cdot CF_2^-$ from (IV) by F^- does not occur and even after heating to 190° starting material (IV) was recovered, albeit in low yield (40%). For comparison compounds (X), (XIV) [obtained from (II) with hexafluoropropene], and (XVI) [obtained from perfluoro-(4-

[9] R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, J. Chem. Soc., 1964, 3736.

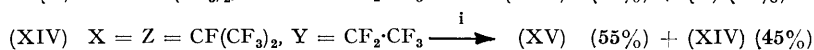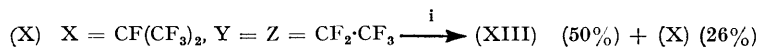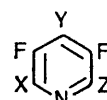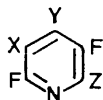[10] R. E. Banks, J. E. Burgess, W. M. Cheng, and R. N. Haszeldine, J. Chem. Soc., 1965, 575.

[11] R. C. Chambers, R. P. Corbally, M. Y. Gribble, and W. K. R. Musgrave, Chem. Comm., 1971, 1345.

isopropylpyridine) (XVII) with tetrafluoroethylene] were heated with caesium fluoride in tetrahydrothiophen dioxide. Compounds (X) and (XIV) rearranged to the corresponding 2,4,6-isomers, (XIII) and (XV) respectively, but the reaction of (XVI) only gave tar. The lack of mobility of a $CF_3 \cdot CF_2$ group in the 5-position is probably attributable to the lower stability of a pentafluoroethyl anion in comparison with a perfluoroisopropyl anion.

Fluoride ion-induced reactions involving hexafluoropropene occur more efficiently with tetrafluoropyridazine

volving bromotrifluoroethylene.[12] It is notable that, in contrast to the results obtained with hexafluoropropene,[6] compounds (XXIII) and (XXIV) were isolated and not the corresponding 3,5- or 3,4,6-isomers and, furthermore, compound (XXIII) was not rearranged on heating with caesium fluoride at 150°. This confirms that reactions of tetrafluoroethylene with tetrafluoropyridazine as well as with pentafluoropyridine (I) involve kinetically controlled processes.

Elemental analysis showed that the high-molecular weight oil contained nitrogen (9·0%), and the n.m.r.

(X)   X = CF(CF_3)_2, Y = Z = CF_2·CF_3 $\xrightarrow{\text{i}}$ (XIII)   (50%) + (X) (26%)

(XIV) X = Z = CF(CF_3)_2, Y = CF_2·CF_3 $\xrightarrow{\text{i}}$ (XV)   (55%) + (XIV) (45%)

(XVI) X = Z = CF_2·CF_3, Y = CF(CF_3)_2 $\xrightarrow{\text{ii}}$ tar

i, CsF, [CH_2]_4SO_2, 160°, 24 h;   ii, CsF, [CH_2]_4SO_2, 180°, 24 h
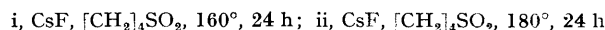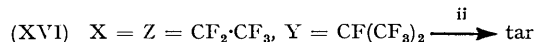
(XXI)[6] than with pentafluoropyridine (I) but, surprisingly, only low yields of pentafluoroethyl derivatives
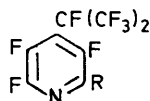
(XVII) R = F
(XVIII) R = CF_3·CF_2
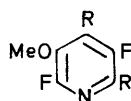
(XIX) R = CF_3·CF_2
(XX)   R = CF(CF_3)_2

(XXII)—(XXIV) were obtained from corresponding reactions of tetrafluoroethylene with tetrafluoropyridazine. Substantial amounts of high molecular weight

(XXI)   (XXII) (13%)

+

(XXIV) (3%)   (XXIII) (8%)
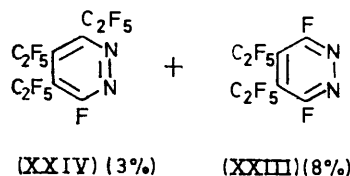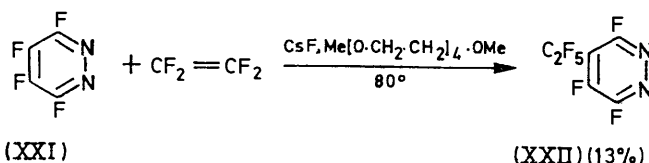
(600—1000) oils were also produced. No perfluorotetraethylpyridazine was isolated although small amounts of the compound were obtained from similar reactions in-

spectrum clearly indicated the presence of pentafluoroethyl groups. This implies that the oil is formed by some process which couples perfluoroalkylated rings, and we suggest that this involves electron transfer from the pentafluoroethyl anion to a pyridazine ring. This proposition gains some support from the fact that solid donor–acceptor complexes are formed from hexafluorobenzene[13,14] with e.g., mesitylene, and highly coloured

A_F = fluorinated pyridazine system.
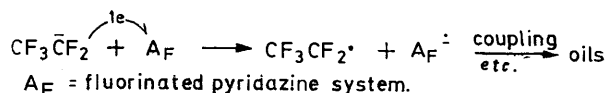
systems are obtained on mixing perfluoroinated heterocyclic compounds with amines or organolithio-compounds.[15] These colours are most easily attributed to electron transfer. Indeed, all the polyfluoroalkylation reactions we have described are accompanied by the formation of coloured (yellow-red) reaction mixtures and the most intense of these colours involve the pyridazine system.

It is interesting that hexafluoropropene[16] reacts much more efficiently than tetrafluoroethylene[17] with cyanuric fluoride. We argued earlier that the perfluoroisopropyl anion will be more stable than the pentafluoroethyl anion, and we would expect the latter to be a better donor in an electron-transfer process. Likewise, we would anticipate that compound (XXI) would be a better acceptor, in electron transfer, than (I). The following probable order of donor capacity, $CF_3 \cdot CF_2^- > CF_3 \cdot CFCl^- > CF_3 \cdot CFBr^- > (CF_3)_2CF^-$, is based on the known effects of halogen or trifluoromethyl attached to a carbanion centre. This

[12] R. D. Chambers and M. Y. Gribble, following paper.
[13] C. R. Patrick and G. S. Prosser, Nature, 1960, 187, 1021.
[14] E. McLoughlin and C. E. Messer, J. Chem. Soc. (A), 1966, 1106.

[15] Unpublished observations made in this laboratory.
[16] R. L. Dressler and J. A. Young, J. Org. Chem., 1967, 32, 2004; U.S.P. 3,525,746/1970.
[17] W. R. Deem, B.P. 1,148,676/1969.

would account for the observation that, in reactions involving tetrafluoropyridazine, chloro- and bromo-trifluoroethylene are more efficient than tetrafluoroethylene, and hexafluoropropene leads to the least amount of high molecular weight oils.

[19]F *N.m.r. Spectra.*—The assignments in the spectra of perfluoro(ethylpyridines) are given in Table 2. The structure of (IV) is clear, since the alternative 2,4,6-isomer would have one fluorine resonance for the 3- and 5-fluorine atoms at *ca.* 104 p.p.m. [calculated from results for compound (III)[18]]. Two resonances are in fact

pyridine (3·0 g, 17·8 mmol) was injected into the flask through a serum cap. The mixture was stirred vigorously and, after 4 h, the volatile material (10·6 g) was transferred from the flask, under high vacuum, to a trap immersed in liquid air. Fractional distillation of this product gave a gaseous component (7·0 g), identified as tetrafluoroethylene by i.r. spectroscopy, and a colourless liquid (3·6 g) which contained compounds (I)—(IV) (g.l.c. analysis).

The residual involatile material from the flask was poured into water (400 ml) and extracted with ether (4 × 25 ml). The combined extracts were washed with water (2 × 10 ml) and dried (MgSO$_4$), and the ether was removed by distill-

TABLE 2

[19]F Chemical shifts of ring fluorine atoms in derivatives of perfluoro-pyridines and -pyridazines (position of the fluorine atom in parentheses)

Compound	Chemical shift from CFCl$_3$ (p.p.m.)	Substituent	Effect of substituent on fluorine-19 shifts (p.p.m.)			Reference compound
			ortho	*meta*	*para*	
(II)	89·0(2,6); 140·3(3,5)	CF$_2$·CF$_3$(4)	−22·3	+0·9		(I)
(III)	83·8(6); 118·5(3); 126·4(5)	CF$_2$·CF$_3$(2)	−21·8	−5·2	−13·9	(II)
(IV)	55·5(6); 115·8(3)	CF$_2$·CF$_3$(5)	−28·3	−2·8		(III)
(X)	53·6(6); 115·2(3)	CF(CF$_3$)$_2$(5)	−30·2	−3·3		(III)
(XIII)	108·6(5); 111·5(3)	CF(CF$_3$)$_2$(6)	−17·8		−7·0	(III)
(XIV)	52·2(6); 113·9(3)	*a*				
(XV)	111·4(3,5)	*a*				
(XVIII)	83·8(6); 115·7(3); 123·3(5)	CF$_2$·CF$_3$(2)	−20·9	−4·3	−13·3	(XVII)
(XVI)	52·9(6); 114·8(3)	CF$_2$·CF$_3$(5)	−30·6	−0·5		(XVIII)
(XIX)	77·8(2); 123·2(5)	MeO(3)	−6·0	+4·7		(III)
(XX)	78·7(2); 120·2(5)	MeO(3)	−4·8	+5·7		(VII)
(XXII)	77·4(3); 97·5(6); 120·6(5)	CF$_2$·CF$_3$(4)	−16·6 [b] −27·0 [c]	+3·5		(XXI)
(XXIII)	77·7(3,6)	CF$_2$·CF$_3$(5)	−19·8	+0·3		(XXII)
(XXIV)	70·2(6)	CF$_2$·CF$_3$(3)			−7·5	(XXIII)

a No disubstituted isomer isolated to allow comparisons.   [b] 3-F.   [c] 5-F.

observed whose shifts are easily assigned on the basis of data for the 2,4,5-isomer (IV); *N.B.* the spectra of perfluoro(ethylpyridines) do not exhibit the temperature dependence which is so pronounced with the perfluoroisopropyl compounds.[18-20] Assignments for the mixed derivatives shown in Table 2 were made on a similar basis.

EXPERIMENTAL

I.r. spectra were measured with a Grubb–Parsons Spectromaster spectrometer and u.v. spectra with a Unicam SP 800. N.m.r. spectra were measured at 40° on a Varian A56/60D (trichlorofluoromethane or tetramethylsilane as external reference). Upfield ^{19}F shifts are quoted as positive. Molecular weights were determined by mass spectrometry with an A.E.I. MS9 instrument. G.l.c. was performed on silicone elastomer–Celite. Tetrahydrothiophen dioxide (THTD) and 2,5,8,11,14-pentaoxapentadecane (POPD) were redistilled *in vacuo* and dried over molecular sieve.

Formation of Perfluoroethylpyridines.—In a typical experiment, a dry flask (see Discussion section) containing caesium fluoride (3·0 g, 20·0 mmol) and POPD (40 ml) was evacuated and heated to *ca.* 80°. The system was charged with tetrafluoroethylene (10·0 g, 100 mmol) from a vacuum system until the bladder was inflated and then pentafluoro-

ation. Distillation of the residue under vacuum gave a small amount of yellow oil (0·4 g), which was similarly analysed by g.l.c., and an intractable tar (0·3 g). The results of several experiments are summarised in Table 1.

Pure samples of compounds (II)—(IV) were separated from the product mixtures by preparative scale g.l.c. (at 80°).

Perfluoro-(4-ethylpyridine) (II) had b.p. 114—115° at 760 mmHg (Found: C, 31·5; F, 64·1%; *M*, 269. C$_7$F$_9$N requires C, 31·2; F, 63·6%; *M*, 269), $\lambda_{max.}$ (cyclohexane) 280·5 nm (log ε 3·59), $\lambda_{max.}$ (film) 6·06w, 6·75s, 7·01, 7·47s, 7·58s, 7·66s, 7·81, 8·0—8·3s, 8·52s, 8·89w, 9·52s, 9·92w, 10·28s, 11·77s, 11·94w, 13·19w, 13·64s, 14·35, 14·96, 18·1—18·5w, and 19·0—19·9w μm, [19]F δ 86·6, (4-CF$_3$) and 113·2 p.p.m. (4-CF$_2$) in addition to data given in Table 2.

Perfluoro-(2,4-diethylpyridine) (III) had b.p. 140—141° at 760 mmHg (Found: C, 29·5; F, 66·5%; *M*, 369. C$_9$F$_{13}$N requires C, 29·3; F, 66·9%; *M*, 369), $\lambda_{max.}$ (cyclohexane) 275·5 nm (log ε 3·68), $\lambda_{max.}$ (film) 6·23w, 6·73s, 6·84s, 7·45s, 7·62s, 7·98—8·25s, 8·25—8·43s, 8·59s, 8·72, 8·99s, 9·50s, 9·90, 11·20s, 12·58w, 13·41, 13·67, 13·84, 14·71w, 15·31w, 15·56w, and 18·2—19·1w μm, [19]F δ 84·9, (2-CF$_3$), 86·6 (4-CF$_3$), 113·5, (4-CF$_2$), and 116·9 p.p.m. (2-CF$_2$).

Perfluoro-(2,4,5-triethylpyridine) (IV) had b.p. 165—166°

[18] R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, 1970, **26**, 71.

[19] R. D. Chambers, L. H. Sutcliffe, and G. J. T. Tiddy, *Trans. Faraday Soc.*, 1970, **66**, 1025.

[20] C. J. Drayton, W. T. Flowers, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1971, 2750.

at 760 mmHg (Found: C, 28·2; F, 68·5%; M, 469. $C_{11}F_{17}N$ requires C, 28·2; F, 68·8%; M, 469), $\lambda_{max.}$ (cyclohexane) 285 nm (log ε 3·81), $\lambda_{max.}$ (film) 6·94s, 7·29w, 7·52s, 7·72, 7·89, 7·98—8·34s, 8·44s, 8·69s, 8·80s, 9·24, 9·60, 9·88s, 10·81w, 11·79s, 13·35, 13·53w, 13·73w, and 14·29w μm, ^{19}F δ 81·4, (4- and 5-CF$_3$), 83·2 (2-CF$_3$), 103·3 (4- and 5-CF$_2$), and 116·0 p.p.m. (2-CF$_2$) (assignments based upon the similarity of the electronic environments of the 4- and 5-pentafluoroethyl groups).

Preparation of Perfluoro-(2,4-diethyl-5-isopropylpyridine) (X).—Caesium fluoride (3·0 g, 20·0 mmol), THTD (35 ml), hexafluoropropene (11·0 g, 73·4 mmol), and compound (III) (4·0 g, 10·8 mmol) were stirred for 1 h at *ca.* 80° and atmospheric pressure (technique as described previously). The volatile products consisted of a little unchanged hexafluoropropene (0·5 g) and a colourless liquid (23·4 g). G.l.c. analysis of the latter indicated the presence of dimers and trimers of the olefin (III), and a single product (X), which was separated by distillation and preparative scale g.l.c. (at 80°), and identified as *perfluoro-(2,4-diethyl-5-isopropylpyridine)* [65% yield based on (II)], b.p. 175° at 760 mmHg (Found: C, 27·6; F, 69·0%; M, 519. $C_{12}F_{19}N$ requires C, 27·8; F, 69·6%; M, 519), $\lambda_{max.}$ (cyclohexane) 286br nm (log ε 3·80), $\lambda_{max.}$ 6·97s, 7·33w, 7·53, 7·71s, 7·9—8·23s, 8·3—8·5s, 8·68s, 8·82s, 9·20, 9·63, 9·80s, 10·28s, 10·85w, 12·10, 13·24, 13·34, 13·50, 13·66w, 13·83w, and 14·06w μm, ^{19}F δ 72·3 (5-CF$_3$), 81·0 (4-CF$_3$), 83·1 (2-CF$_3$), 100·1 (4-CF$_2$), 116·1 (2-CF$_2$), and 170·2 p.p.m. (5-CF).

Preparation of Perfluoro-(4-ethyl-2,5-di-isopropylpyridine) (XIV).—A reaction similar to that just described, with fluoride (3·0 g, 20·0 mmol), THTD (35 ml), hexafluoropropene (16·0 g, 106·5 mmol), and (II) (5·0 g, 18·6 mmol), at *ca.* 75° for 40 min, gave a little unchanged hexafluoropropene (0·5 g) and a colourless liquid (19·5 g). G.l.c. analysis of the latter indicated the presence of dimers and trimers of the olefin and a single product, which was separated by distillation and identified as *perfluoro(4-ethyl-2,5-di-isopropylpyridine)* (XIV) [quantitative yield based on (II)], b.p. 176° at 760 mmHg (Found: C, 27·1; F, 70·7%; M, 569. $C_{13}F_{21}N$ requires C, 27·4; F, 70·3%; M, 569), $\lambda_{max.}$ (cyclohexane) 286br nm (log ε 3·83), $\lambda_{max.}$ 7·0s, 7·37w, 7·63—7·84s, 7·9—8·2s, 8·42s, 8·58, 8·70, 8·76, 9·17, 9·62, 9·88, 10·18, 10·31, 11·00w, 12·13, 13·31, 13·48, 14·21w, and 15·04w μm, ^{19}F δ 72·3 (5-CF$_3$), 74·1 (2-CF$_3$), 80·3 (4-CF$_3$), 99·7 (4-CF$_2$), 170·5 (5-CF), and 183·8 p.p.m. (2-CF).

Tetrafluoroethylene and Perfluoro-(4-isopropylpyridine) (XVII).—Caesium fluoride (4·0 g, 26·3 mmol), POPD (30 ml), tetrafluoroethylene (5·0 g, 50·0 mmol), and (XVII) [4] (4·1 g, 12·9 mmol) were stirred for 4 h at *ca.* 80° and at atmospheric pressure as already described. Unchanged tetrafluoroethylene (2·5 g) and a colourless liquid (2·9 g) were recovered on transfer of the volatile material, under high vacuum, from the reaction flask. G.l.c. analysis of the latter showed unchanged (XVII) and three products, which were separated by preparative scale g.l.c. (at 80°).

Perfluoro-(2-ethyl-4-isopropylpyridine) (XVIII) [25% yield based on (XVII)] had b.p. 158° at 760 mmHg (Found: C, 28·4; F, 67·5%; M, 419. $C_{10}F_{15}N$ requires C, 28·7; F, 68·0%; M, 419), $\lambda_{max.}$ (cyclohexane) 274·5 nm (log ε 3·68), $\lambda_{max.}$ 6·26w, 6·74s, 6·84s, 7·16w, 7·44s, 7·69s, 7·82—8·20s, 8·38s, 8·71, 9·00, 9·32, 9·47, 9·86, 10·19s, 11·22, 11·51, 13·31, 13·50—13·91, 14·03w, 14·12w, 15·23, and 18·20—19·00w μm, ^{19}F δ 75·1 (4-CF$_3$), 83·5 (2-CF$_3$), 115·0 (2-CF$_2$), and 180·0 p.p.m. (4-CF).

Perfluoro-(2,5-diethyl-4-isopropylpyridine) (XVI) [13%

yield based on (XVII)] had b.p. 170° at 760 mmHg (Found: C, 27·6; F, 69·3%; M, 519. $C_{12}F_{19}N$ requires C, 27·8; F, 69·6%; M, 519), $\lambda_{max.}$ (cyclohexane) 285br nm (log ε 3·79), $\lambda_{max.}$ 6·90s, 6·99s, 7·52s, 7·70s, 7·90—8·26s, 8·50s, 8·70s, 8·79s, 9·24, 9·53w, 9·87s, 10·25, 10·91w, 11·95, 13·32, 13·55, 13·70, 13·82, and 14·38w μm, ^{19}F δ 72·1 (4-CF$_3$), 80·1 (5-CF$_3$), 83·0 (2-CF$_3$), 100·0 (5-CF$_2$), 116·3 (2-CF$_2$), and 170·1 p.p.m. (4-CF).

Perfluoro-(2,5,6-triethyl-4-isopropylpyridine) [2% yield based on (XVII)] had b.p. 185° at 760 mmHg (Found: C, 27·4; F, 70·0%; M, 619. $C_{14}F_{23}N$ requires C, 27·1; F, 70·6%; M, 619), $\lambda_{max.}$ 6·39w, 6·96, 7·6—8·9s, 9·32, 9·51s, 9·95s, 10·22s, 10·48, 11·25, 13·30s, 13·56, 13·95w, 14·14w, 14·3—14·5, 15·08w, and 18·2—18·9w μm, ^{19}F δ 73·9, 81·4, 84·8, 108·7, 117·3, and 171·9 p.p.m. (complex bands which could not be fully analysed). The absence of an absorption at 40—50 p.p.m., calculated from substituent chemical shifts, indicated that the 6, and not the 3, fluorine atom in (XVI) is replaced on further substitution.

Reaction of Perfluoro-(2,4-diethylpyridine) (III) *with Sodium Methoxide.*—A solution of sodium (0·031 g, 1·35 mmol) in methanol (32 ml) was added to a stirred solution of (III) (0·5 g, 1·35 mmol) in methanol (30 ml) during 1 h at *ca.* 20 or 70°. The mixture was stirred for a further 3 h, then poured into water (300 ml) and extracted with methylene chloride (4 × 25 ml). The combined extracts were dried (MgSO$_4$) and evaporated to leave a pale yellow liquid (0·45 g). G.l.c. analysis showed a single component, 2,5-*difluoro-3-methoxy-4,6-bispentafluoroethylpyridine* (XIX) [85% yield based on (III)], b.p. 195—196° at 760 mmHg (Found: C, 31·2; H, 1·0; F, 59·8%; M, 381. $C_{10}H_3F_{12}NO$ requires C, 31·5; H, 0·8; F, 59·8%; M, 381), $\lambda_{max.}$ (cyclohexane) 286 nm (log ε 3·70), $\lambda_{max.}$ 3·76w, 6·18w, 6·28w, 6·70s, 6·86s, 6·95, 7·18, 7·43s, 7·61s, 7·81, 8·0—8·4s, 8·65, 8·93s, 9·46, 9·56s, 10·53, 11·45, 12·57w, 13·36, 13·70, 13·83, 14·12w, 14·73w, and 18·2—19·1w μm, ^{19}F δ 85·5 (6-CF$_3$), 86·4 (4-CF$_3$), 116·4 (4-CF$_2$), and 117·2 p.p.m. (6-CF$_2$), ^1H δ 3·9 (OCH$_3$).

Reaction of Perfluoro-(2,4-di-isopropylpyridine) (VII) *with Sodium Methoxide.*—Two similar reactions at *ca.* 20 and 85° between (VII) (0·5 g, 1·07 mmol) in methanol (30 ml) and a solution of sodium (0·025 g, 1·09 mmol) in methanol (23·5 ml) gave a pale yellow liquid (0·45 g). G.l.c. analysis showed a single component, 2,5-*difluoro-3-methoxy-4,6-bisheptafluoroisopropylpyridine* (XX) [88% yield based on (VII)], b.p. 199—200° at 760 mmHg (Found: C, 29·7; H, 0·6; F, 63·1%; M, 481. $C_{12}H_3F_{16}NO$ requires C, 29·9; H, 0·6; F, 63·2%; M, 481), $\lambda_{max.}$ (cyclohexane) 286 nm (log ε 3·75), $\lambda_{max.}$ 3·37w, 6·25w, 6·71s, 6·89s, 7·00s, 7·23w, 7·6—8·2s, 8·3s, 8·47s, 8·56s, 8·75, 8·87, 9·35s, 9·74, 10·22s, 10·64w, 10·83w, 11·55, 11·79w, 12·89w, 13·32, 13·42, 13·65, 13·83s, 14·4—14·8w, 15·4w, 15·6, and 18·2—19·2 μm, ^{19}F δ 76·2 (CF$_3$) 179·6 and 185·5 p.p.m. (tert. F), ^1H δ 3·8 (OCH$_3$).

Attempted Rearrangement of Perfluoro-(2,4,5-triethylpyridine) (IV).—(*a*) A mixture of (IV) (3·0 g, 6·4 mmol), caesium fluoride (3·0 g, 20·0 mmol), and THTD (30 ml) in a nickel tube (80 ml capacity) was heated, with rotational agitation, in an oil-bath at 160°, for 16 h. The volatile material was transferred under high vacuum into a trap immersed in liquid air. The condensate (2·6 g) was analysed by ^{19}F n.m.r., g.l.c., and i.r. spectroscopy, and identified as unchanged (IV). The residue in the tube was poured into water (400 ml) and extracted with ether (4 × 20 ml). Drying (MgSO$_4$) and evaporation gave an intractable tar (0·5 g).

(b) Reaction (a) was repeated, in the presence of hepta-fluoroquinoline (3·0 g, 11·8 mmol), with a mixture of (IV) (1·2 g, 2·6 mmol), caesium fluoride (3·0 g, 20·0 mmol), and THTD (30 ml) heated to 160° over 72 h. The volatile products comprised a pale yellow liquid (0·9 g) and a white crystalline solid (2·7 g) which were identified as (IV) and heptafluoroquinoline respectively by i.r. and ^{19}F n.m.r. spectroscopy. Extraction of the residue gave no tractable products.

(c) Reaction (a) was repeated with identical amounts of materials heated to 190° over 18 h. Analysis of the recovered volatile material (1·2 g) by ^{19}F n.m.r. showed unchanged (IV). Extraction of the residue gave an intractable tar (3·5 g).

Rearrangement of Perfluoro-(2,4-diethyl-5-isopropylpyridine) (X) *to Perfluoro-(2,4-diethyl-6-isopropylpyridine)* (XIII).—A mixture of (X) (2·0 g, 3·9 mmol), caesium fluoride

19·1w μm, ^{19}F δ 74·5 (2,6-CF$_3$), 85·5 (4-CF$_3$), 112·3 (4-CF$_2$), and 185·2 p.p.m. (2,6-CF).

Attempted Rearrangement of Perfluoro-(2,5-diethyl-4-isopropylpyridine) (XVI). A mixture of (XVI) (2·0 g, 3·9 mmol), caesium fluoride (3·0 g, 20·0 mmol), and THTD (20 ml) in a nickel tube (80 ml capacity) was heated, with rotational agitation, in an oil-bath at 180°, for 24 h. The mixture was worked up in the usual manner; however, only an intractable tarry residue (0·8 g) was obtained.

Formation of Perfluoroethylpyridazines.—By a similar procedure to that already described above, with caesium fluoride (3·0 g, 20·0 mmol) and POPD (35 ml), compounds (XXII)—(XXIV) were obtained and separated by preparative scale g.l.c. (at 80°). The results are summarised in Table 3.

Perfluoro-(4-ethylpyridazine) (XXII) had b.p. 144° at 760 mmHg (Found: C, 28·3; F, 60·6%; M, 252. C$_6$F$_8$N$_2$

TABLE 3

Fluoride ion-induced reaction between tetrafluoropyridazine and tetrafluoroethylene

Reaction time (h)	Temp. (°C)	(XXI)	CF$_2$=CF$_2$ Initially	Recovered (g)	Volatile products (g)	Residue (g)	Yields (%) * (XXII)	(XXIII)	(XXIV)	Conversion (%)
1	80	3·0 g 20·0 mmol	10·0 g 100·0 mmol	9·0	2·7	0·9	37	7		45
2	80	3·0 g 20·0 mmol	10·0 g 100·0 mmol	8·5	2·1	1·9	21	11	2	94
3	80	3·0 g 20·0 mmol	10·0 g 100·0 mmol	7·5	1·7	2·85	13	8	3	100
4	80	3·0 g 20·0 mmol	10·0 g 100·0 mmol	7·0	1·35	4·2	9	6	5	100
5	80	3·0 g 20·0 mmol	10·0 g 100·0 mmol	7·0	0·75	4·9	4	3	4	100
6	25	4·5 g 29·6 mmol	5·0 g 50·0 mmol	4·0	4·5	0·35	<3			<5
96	25	3·2 g 21·1 mmol	8·0 g 80·0 mmol	2·5	1·0	7·0	4	4	4	98

* Based on weight of (XXI) consumed.

(1·0 g, 6·7 mmol), and THTD (10 ml) in a Carius tube (75 ml capacity) was heated, with rotational agitation, in an oil-bath at 160°, for 24 h. G.l.c. analysis of the recovered volatile material (1·3 g) showed unchanged (X) and a single product (XIII), which was separated by preparative scale g.l.c. (at 80°). *Perfluoro-(2,4-diethyl-6-isopropylpyridine)* (XIII) [52% yield based on (X)] had b.p. 168—169° at 760 mmHg (Found: C, 27·5; F, 69·2%; M, 519. C$_{12}$F$_{19}$N requires C, 27·8; F, 69·6%; M, 519), λ$_{max.}$ (cyclohexane) 274br nm (log ε 3·63), λ$_{max.}$ 6·24, 6·83, 7·43s, 7·58s, 7·78s, 7·9—8·2s, 8·3—8·5s, 8·75s, 8·96, 9·4s, 9·48s, 9·91w, 10·14s, 10·35w, 13·27w, 13·51w, 13·6, 13·5—15·1w, and 18·3—19·0w μm, ^{19}F δ 76·4 (6-CF$_3$), 85·2 (2-CF$_3$), 87·4 (4-CF$_3$), 113·5 (4-CF$_2$), 116·8 (2-CF$_2$), and 186·9 p.p.m. (6-CF).

Rearrangement of Perfluoro-(4-ethyl-2,5-di-isopropylpyridine) (XIV) *to Perfluoro-(4-ethyl-2,6-di-isopropylpyridine)* (XV).—An identical experiment with (XIV) (2·0 g, 3·5 mmol), caesium fluoride (1·0 g, 6·7 mmol), and THTD (10 ml) gave a volatile material (1·5 g) which consisted of un-changed (XIV) and a single product, *perfluoro-(4-ethyl-2,6-di-isopropylpyridine)* (XV) [54% yield based on (X)], b.p. 180° at 760 mmHg (Found: C, 26·9; F, 70·0%; M, 569. C$_{13}$F$_{21}$N requires C, 27·4; F, 70·3%; M, 569), λ$_{max.}$ (cyclohexane) 274 nm (log ε 3·66), λ$_{max.}$ 6·27w, 6·88, 7·47, 7·60s, 7·8—8·2s, 8·51s, 8·75, 8·89w, 9·44s, 9·99w, 10·19s, 10·44w, 13·25, 13·60, 13·70, 13·81, 14·58, 14·81w, 15·82w, and 18·2—

requires C, 28·5; F, 60·4%; M, 252), λ$_{max.}$ (cyclohexane) 262·5 nm (log ε 3·41), λ$_{max.}$ (film) 6·14, 6·32s, 6·78s, 6·99s, 7·46s, 7·62s, 8·14br,s, 8·49s, 8·63s, 9·05s, 9·28s, 9·77s, 11·48s, 12·92w, 13·15s, 13·56, and 14·67 μm, ^{19}F δ 87·0 (CF$_3$) and 115·0 p.p.m. (CF$_2$).

Perfluoro-(4,5-diethylpyridazine) (XXIII) had m.p. 37—37·5° (Found: C, 27·5; F, 64·2%; M, 352. C$_8$F$_{12}$N$_2$ re-quires C, 27·3; F, 64·8%; M, 352), λ$_{max.}$ (cyclohexane) 277 and 285·5infl nm (log ε 3·698 and 3·649), λ$_{max.}$ (film) 7·01s, 7·52s, 7·80, 8·13br,s, 8·55s, 8·83s, 9·46, 9·79s, 11·02s, 11·80s, 13·09s, 13·32s, 13·77s, and 14·46 μm, ^{19}F δ 82·6 (4- and 5-CF$_3$) and 107·2 p.p.m. (4- and 5-CF$_2$).

Perfluoro-(3,4,5-triethylpyridazine) (XXIV) had b.p. 174—175° at 760 mmHg (Found: C, 26·3; F, 66·7%; M, 452. C$_{10}$F$_{16}$N$_2$ requires C, 26·5; F, 67·3%; M, 452), λ$_{max.}$ (cyclo-hexane) 268 nm (log ε 3·498), λ$_{max.}$ (film) 6·46, 7·04 s, 7·57s, 7·70s, 7·85s, 8·00—8·60s, 8·68s, 8·84s, 9·00s, 9·49s, 9·81s, 11·18s, 13·15, 13·29, 13·68s, 14·43, and 14·73 μm, ^{19}F δ 81·0 (4- and 5-CF$_3$) and 74·5 (3-CF$_3$), and 93·0br, 104·7br, and 108·0br p.p.m. (CF$_2$ groups).