

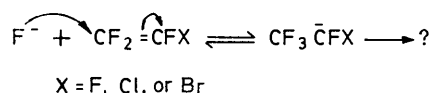
## Reactions Involving Fluoride Ion. Part VII.<sup>1</sup> Reactions of Polyfluoroethylenes with Pentafluoropyridine and Tetrafluoropyridazine †

By Richard D. Chambers\* and Michael Y. Gribble, Department of Chemistry, University Science Laboratories, South Road, Durham

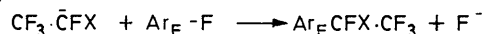
Reactions induced by fluoride ion of the olefins  $CF_2=CFX$  ( $X = Cl, Br, \text{ or } H$ ) with pentafluoropyridine (I) and with tetrafluoropyridazine (VII) are described. With chlorotrifluoroethylene, pentafluoroethyl and chlorotetrafluoroethyl derivatives were obtained. A pseudo- $S_N2'$  process, involving attack of fluoride ion at the aromatic ring, is proposed as the mechanism for the displacement of chloride ion. This was confirmed by a reaction involving cyanuric fluoride. Reaction with bromotrifluoroethylene led to pentafluoroethyl derivatives in the case of the pyridazine (VII), *via* polyfluoroalkylation, but a more complex exchange reaction occurred with the pyridine (I). Reactions with trifluoroethylene gave mainly tars, although a small amount of a product arising from proton abstraction was isolated. Reactions with 1,1-dichlorodifluoroethylene gave products similar to those obtained with chlorotrifluoroethylene in the case of the pyridazine (VII) but no reaction occurred with the pyridine (I).

It is well established that carbanions generated by reaction of perfluoro-olefins with fluoride ion will react with polyfluoroaromatic compounds, to give perfluoroalkyl derivatives<sup>2</sup> but there is only our preliminary report of similar reactions involving polyfluoro-olefins like chloro- or bromo-trifluoroethylene.<sup>3</sup> Indeed, only limited information is available<sup>4-6</sup> on the reaction of fluoride ion with these olefins. We have investigated several fluoride ion-induced reactions of bromo- and chloro-trifluoroethylene and of trifluoroethylene itself.

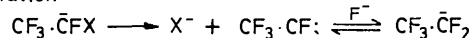
The complexities of the systems are probably most easily appreciated if some of the possible fates of the intermediate carbanions are set out (Scheme 1). Polyfluoroalkylation (I) has been observed in reactions of



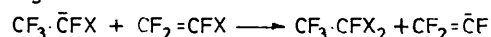
(1) Polyfluoroalkylation



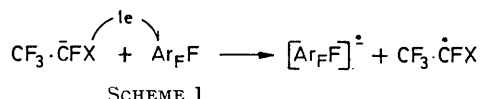
(2) Carbene formation



(3) Halogen exchange



(4) Charge transfer



hexafluoropropene or tetrafluoroethylene<sup>1,2</sup> with several activated polyfluoroaromatic systems, but in the reaction

between tetrafluoroethylene and tetrafluoropyridazine polymers were the major products, and this was attributed to the occurrence of a charge-transfer process (4).<sup>1</sup> Fluoride ion-induced reactions were carried out in an apparatus, operating at atmospheric pressure, which is described in the preceding paper.<sup>1</sup> Chlorotrifluoroethylene reacted with pentafluoropyridine (I) at 90° in tetrahydrothiophen dioxide (THTD) or 2,5,8,11,14-pentaoxapentadecane (POPD) and some of the results are shown in Scheme 2. Polyfluoroalkylation occurs in both cases but is accompanied by loss of chlorine and the effect of solvent is marked in that much more chlorine is lost when THTD is used. The reasons for this difference, however, are not obvious. It is possible to put forward several mechanisms for the displacement of chlorine by fluorine but we must be able to account for the fact that no compounds were isolated which contained more than one polyfluoroalkyl group and also contained chlorine. The most obvious possibility, direct displacement from the olefin (Scheme 3), is unlikely because nucleophilic attack on chlorotrifluoroethylene invariably occurs at the difluoromethylene group.<sup>7</sup> Also, no tetrafluoroethylene or derived oligomers<sup>8,9</sup> were observed; furthermore, the reaction with pentafluoropyridine occurred more rapidly than the corresponding reaction with tetrafluoroethylene itself.<sup>1</sup>

The chloride ion produced in the reaction of chlorotrifluoroethylene with pentafluoropyridine (I) is particularly reactive, as shown by the fact that 4-chlorotetrafluoropyridine (V) is produced by displacement of fluorine from (I) by chlorine. Reaction of caesium or potassium chloride directly with (I) gives (V) only under forcing conditions.<sup>10</sup>

Surprisingly, reaction with tetrafluoropyridazine (VII) gave no chlorotetrafluoroethyl derivatives at all, but only

† Presented at the 6th International Symposium on Fluorine Chemistry, Durham, July 1971.

<sup>1</sup> R. D. Chambers and M. Y. Gribble, preceding paper.

<sup>2</sup> See earlier parts of the series and references therein.

<sup>3</sup> R. D. Chambers, R. A. Storey, and W. K. R. Musgrave, *Chem. Comm.*, 1966, 384.

<sup>4</sup> W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091.

<sup>5</sup> C. G. Krespan, *J. Org. Chem.*, 1962, **27**, 1813.

<sup>6</sup> W. T. Miller and R. Becker, Abstracts of Papers, 145th Meeting, American Chemical Society, New York, September 1963, p. 14M.

<sup>7</sup> R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, 1965, **4**, 50, and references therein.

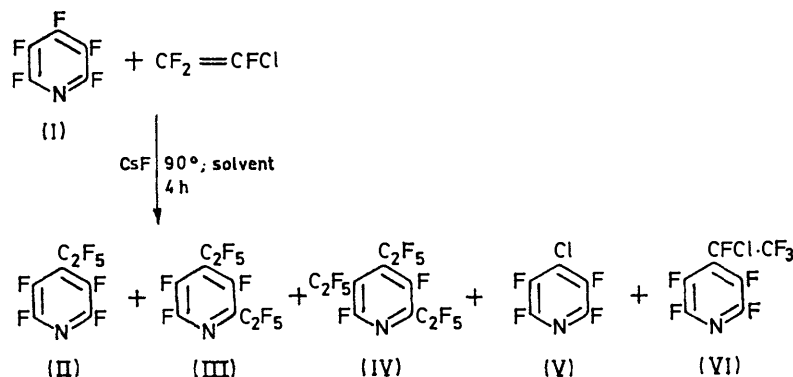
<sup>8</sup> D. P. Graham, *J. Org. Chem.*, 1966, **31**, 955.

<sup>9</sup> H. C. Fielding and A. J. Rudge, B.P. 1,082,127/1967.

<sup>10</sup> D. Lomas and S. Partington, unpublished results.

pentafluoroethyl compounds, together with some polymer. The polymer is probably produced by a process involving electron transfer [see (4), Scheme 1], similar to that which has been put forward previously to account

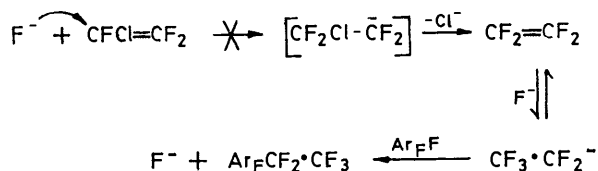
philic attack at the ring. A benzylic-type displacement process was considered because reaction of the chlorotetrafluoroethyl derivative (VI) with caesium fluoride produces the pentafluoroethyl compound (II), at 90°.



Solvent		Yields (%)				
THTD	15	4	3	4	15	
POPD	0	6	4	8	46	

SCHEME 2

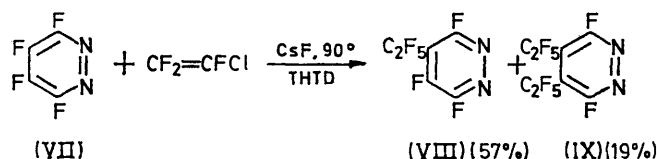
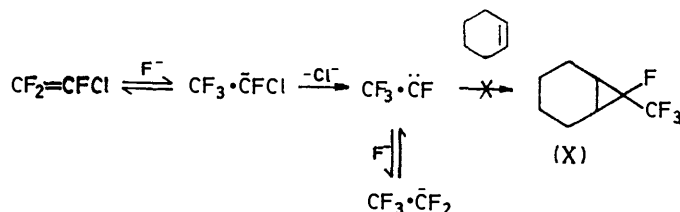
for a high molecular weight product obtained from tetrafluoroethylene with (VII).<sup>1</sup>



SCHEME 3

A carbene process [(2), Scheme 1] for loss of chlorine cannot be ruled out, but we were unable to detect any norcarane derivative (X) when chlorotrifluoroethylene

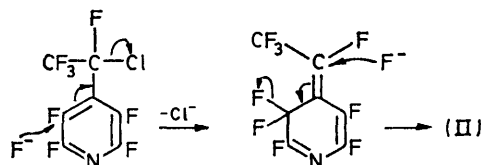
Such a process could involve more bond making than bond breaking at the transition state where, as has been pointed out, electron-withdrawing substituents in the ring would enhance the reaction rate.<sup>11</sup> This could account for most other characteristics so far observed. However, there is a much more likely process, similar to that proposed by Kobayashi for displacement of fluorine



reacted with fluoride ion in the presence of an excess of cyclohexene. However, fluoride ion may compete more successfully for the carbene than cyclohexene.

Nevertheless, we have yet to account for the fact that substituents remote from the chlorotetrafluoroethyl group influence the ease of displacement of chlorine, *i.e.* no chlorine remains in the side chain in either the poly-substituted pyridines or the substituted pyridazines. These substituent effects are more consistent with nucleo-

philic attack at the ring.<sup>12-14</sup> from 3-trifluoromethylquinoline,<sup>12-14</sup> which involves a pseudo-S<sub>N</sub>2' sequence. Since this process would involve nucleophilic attack at the ring then it is particularly in



keeping with the observed substituent effects. Furthermore, reaction of chlorotrifluoroethylene with cyanuric fluoride (XI) gave only a chlorotetrafluoroethyl com-

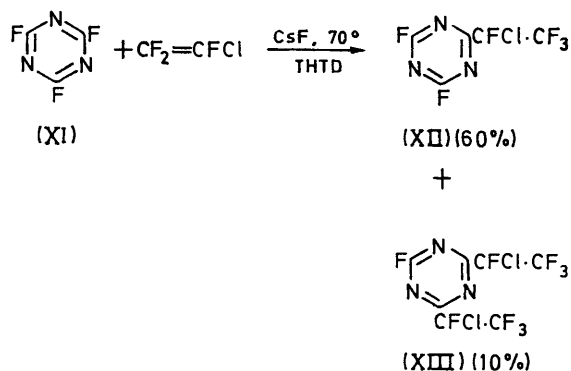
<sup>11</sup> C. G. Swain and W. P. Langsdorf, *J. Amer. Chem. Soc.*, 1951, **73**, 2813.

<sup>12</sup> Y. Kobayashi, I. Kumadaki, S. Taguchi, and Y. Hanzawa, *Tetrahedron Letters*, 1970, 3901.

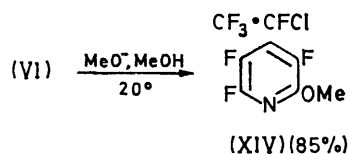
<sup>13</sup> Y. Kobayashi, I. Kumadaki, and S. Taguchi, *Chem. and Pharm. Bull. (Japan)*, 1971, **19**, 624; 1972, **20**, 823.

<sup>14</sup> Y. Kobayashi, I. Kumadaki, S. Taguchi, and Y. Hanzawa, *Chem. and Pharm. Bull. (Japan)*, 1972, **20**, 1047.

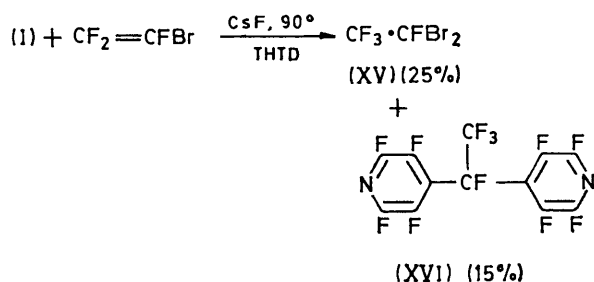
pound (XII) at 70°, which did not undergo chlorine-fluorine exchange with caesium fluoride up to 110°. This



confirms the operation of the pseudo-S<sub>N</sub>2' process because neither (XII) nor (XIII) has carbon atoms available which are *ortho* or *para* to the chlorotetrafluoroethyl groups, for attack by fluoride ion. Nevertheless, reaction of (VI) with methoxide ion leads to substitution of fluorine atoms in the ring rather than replacement of chlorine.



The reaction of bromotrifluoroethylene with pentafluoropyridine (I) took a different course. Polymeric material was produced, together with small amounts of 1,1-dibromotetrafluoroethane (XV). It is clear that the initial anion formed from bromotrifluoroethylene in this



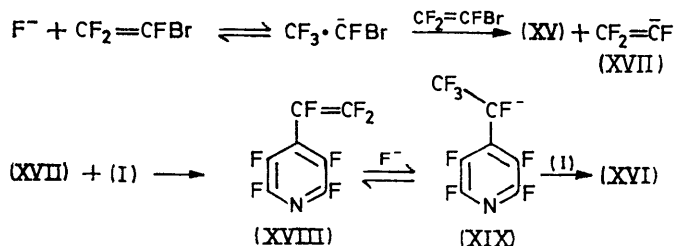
case undergoes exchange for bromine with the olefin [see (3), Scheme 1] to give a vinyl anion (XVII). An exchange process has been proposed by Miller and Becker<sup>6</sup> to account for the products obtained from the reaction of 1,1-dichlorodifluoroethylene with fluoride ion. The anion (XVII) would react with (I) to give a vinylpyridine (XVIII), which could itself react with fluoride ion to give

<sup>15</sup> R. D. Chambers and M. Y. Gribble, in preparation.

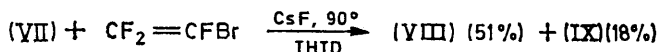
<sup>16</sup> A. J. Parker, *Quart. Rev.*, 1962, **16**, 163; J. Hayami, N. Ono, and A. Kaji, *Tetrahedron Letters*, 1968, 1385; I. N. Rozhkov and I. L. Knunyants, *Doklady Akad. Nauk S.S.S.R.* (English trans.), 1971, **199**, 622.

the anion (XIX) which, in turn, would form the observed product (XVI) by reaction with pentafluoropyridine (I). This mechanism was confirmed by reaction of (XVIII), obtained independently,<sup>15</sup> with fluoride ion and (I) under similar conditions; compound (XVI) was obtained in 60% yield.

In contrast, reaction of bromotrifluoroethylene with tetrafluoropyridazine (VII) gave only pentafluoroethyl

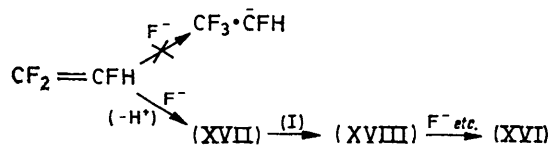


derivatives, *i.e.* the reaction was analogous to that with chlorotrifluoroethylene. With longer reaction times or



higher temperatures, small amounts of perfluoro-tri- and -tetra-ethylpyridazines were obtained (see Experimental section) which were difficult to obtain from corresponding reactions with tetrafluoroethylene.<sup>1</sup> Thus in the case of bromotrifluoroethylene there is competition between polyfluoroalkylation and bromine exchange [see (1) and (3), Scheme 1]. With pentafluoropyridine (I) exchange occurs but, with the more reactive pyridazine system, polyfluoroalkylation is favoured.

Trifluoroethylene gave only tars with tetrafluoropyridazine (VII) and a trace of (XVI) with pentafluoropyridine (I). This almost certainly arises from proton abstraction from the olefin by fluoride ion, which is a very strong base in an aprotic medium,<sup>16</sup> rather than from fluoride addition.

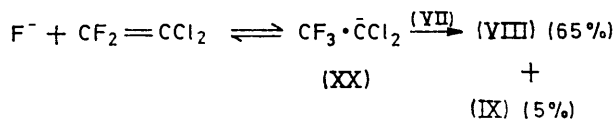


Thus, most of the possibilities outlined in Scheme 1 have been observed, except the carbene process (2) for which there is, so far, no evidence.

1,1-Dichlorodifluoroethylene gives products similar to those obtained by use of chlorotrifluoroethylene with tetrafluoropyridazine (VII), but no reaction occurred with pentafluoropyridine (I). These observations are consistent with the mechanistic proposals which we have already made for reactions involving the trifluoroethylenes. Chlorine leads to a more stable system than fluorine when directly attached to a carbanion centre,<sup>17</sup>

<sup>17</sup> J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Amer. Chem. Soc.*, 1957, **79**, 1406.

and this would account for the greater reactivity of chlorotrifluoroethylene than 1,1-dichlorodifluoroethylene with the pyridine (I). With the more reactive pyridazine



(VII), attack by the anion (XX) takes place, followed by replacement of chlorine by fluorine *via* the pseudo- $\text{S}_\text{N}2'$

8·84, 9·51, 10·24s, 10·68s, 12·36s, 13·18, 13·76, 13·91s, and 14·38s  $\mu\text{m}$ ,  $^{19}\text{F}$   $\delta$  82·1 (CF<sub>3</sub>), 88·6 (2- and 6-F), 125·0 (CF), and 137·3 p.p.m. (3- and 5-F) (ratio 3 : 2 : 1 : 2),  $J_{\text{CF}_3, \text{CF}}$  8,  $J_{\text{CF}_3, 5\text{-F}}$  10 Hz.

The residual involatile material from the reaction flask was poured into water (400 ml) and extracted with ether (4 × 25 ml), and the combined extracts were washed with water (2 × 10 ml) and dried (MgSO<sub>4</sub>). The ether was removed by distillation. Distillation of the residue under vacuum gave a small amount of a yellow oily liquid which did not contain any identifiable products. The results of several experiments are summarised in Table 1.

TABLE 1

Solvent	Reaction time (h)	CF <sub>2</sub> =CFCl		Volatile product (g)	Residue (g)	(II)	Yields (%) *				Conversion (%)
		Initially	Recovered (g)				(III)	(IV)	(V)	(VI)	
THTD	4	9·0 g 77·2 mmol	2·0	2·3	0·8	51	4	3	4	15	78
THTD	24	12·0 g 103 mmol	3·0	3·1	1·0	19	8	8	5	17	82
POPD	4	8·0 g 68·6 mmol	1·8	3·2	1·2		6	4	8	46	67
POPD	24	9·0 g 77·2 mmol	1·9	3·1	1·0		5	8	9	40	76

\* Based on C<sub>5</sub>F<sub>5</sub>N consumed.

TABLE 2

Solvent	(VII)	CF <sub>2</sub> =CFCl		Volatile product (g)	Yields (%) *		Conversion (%)
		Initially	Recovered (g)		(VIII)	(IX)	
THTD	4·0 g 26·3 mmol	8·0 g 68·6 mmol	5·0	5·3	57	19	58
POPD	4·0 g 26·3 mmol	10·0 g 85·8 mmol	2·0	4·2	41	9	53

\* Based on C<sub>4</sub>F<sub>4</sub>N<sub>2</sub> consumed.

process already outlined, giving pentafluoroethyl derivatives, (VIII) and (IX).

#### EXPERIMENTAL

For general remarks see preceding paper.

*Reactions Involving Chlorotrifluoroethylene.*—(a) *With pentafluoropyridine* (I). The simple apparatus used is described in the preceding paper.<sup>1</sup> In a typical experiment, a dry flask containing caesium fluoride (3·0 g, 20·0 mmol) and THTD (35 ml) was evacuated and then heated to *ca.* 90°. The system was then charged with chlorotrifluoroethylene (9·0 g, 77·2 mmol) from a vacuum system until the bladder was inflated, after which compound (I) (3 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 (4·3 g) was transferred under high vacuum to a flask contained in liquid air. Fractional distillation of this product gave a gaseous component (2·0 g), identified as chlorotrifluoroethylene by i.r. spectroscopy, and a colourless liquid (2·3 g) which contained compounds (I)—(VI). Quantitative analysis of the mixture was carried out by analytical scale g.l.c. (gas-density balance), and samples were separated with a preparative scale instrument (silicone elastomer on Celite; 80°). Compounds (II)—(V) were identified by spectral comparison with authentic samples obtained previously by other methods,<sup>1,18</sup> and 4-(1-chlorotetrafluoroethyl)tetrafluoropyridine (VI) was obtained as a liquid (Found: C, 29·8; Cl, 11·9; F, 53·5. C<sub>7</sub>ClF<sub>8</sub>N requires C, 30·1; Cl, 12·5; F, 53·2%), b.p. 140°,  $\lambda_{\text{max}}$  6·06, 6·75s, 7·00, 7·77s, 8·11s, 8·25s,

(b) *With tetrafluoropyridazine.* By use of a procedure similar to that described in (a), compounds (VIII) and (IX) were obtained and identified spectroscopically.<sup>1</sup> The results are summarised in Table 2.

(c) *With cyanuric fluoride* (XI). Caesium fluoride (3·0 g, 20·0 mmol), sulpholan (30 ml), cyanuric fluoride (XI) (19·0 g, 140·0 mmol), and chlorotrifluoroethylene (24·0 g, 206·0 mmol) were stirred at atmospheric pressure for 24 h at 30°, followed by 88 h at 55° and finally 88 h at 70°. The volatile products consisted of unchanged olefin (2·0 g) and a colourless liquid (23·0 g). G.l.c. analysis of the latter showed unchanged (XI) (60% recovery) as well as a major and a minor product. The components were separated by distillation at atmospheric pressure and the major product was identified as 2-(1-chlorotetrafluoroethyl)-4,6-difluoro-s-triazine (XII) (60%), b.p. 128—129° at 760 mmHg (Found: C, 23·2; Cl, 14·6; F, 44·8%; *M*, 251 and 253. C<sub>5</sub>ClF<sub>6</sub>N<sub>3</sub> requires C, 23·8; Cl, 14·1; F, 45·3%; *M*, 251 and 253),  $\lambda_{\text{max}}$  6·20s, 6·28s, 6·37s, 6·77s, 6·90, 6·93, 7·09s, 7·68, 8·06s, 8·22s, 8·64, 9·19, 9·50s, 10·51, 11·80s, 12·18s, 13·47, 14·50w, 17·39w, and 18·15w  $\mu\text{m}$ ,  $^{19}\text{F}$   $\delta$  31·9br (s, 4- and 6-F), 79·9 (CF<sub>3</sub>), and 133·7 p.p.m. (CFCl) (ratio 2 : 3 : 1),  $J_{\text{CF}, \text{CF}_3}$  6·5 Hz. The mass spectrum of the minor component, contaminated with (XII), indicated the presence of the disubstituted compound (XIII), *m/e* 367 (C<sub>7</sub>Cl<sub>2</sub>F<sub>8</sub>N<sub>3</sub><sup>+</sup>) and 298 (loss of Cl<sub>2</sub>).

*Reactions Involving Bromotrifluoroethylene.*—(a) *With pentafluoropyridine* (I). A mixture of caesium fluoride (3·0 g, 20·0 mmol), THTD (35 ml), compound (I) (3·0 g, 17·8

<sup>18</sup> H. C. Fielding, B.P. 1,133,492/1968.

mmol), and bromotrifluoroethylene (16.0 g, 100 mmol) was stirred for 2 h at 90° and atmospheric pressure. Removal of volatile material under vacuum gave bromotrifluoroethylene (5.0 g), identified spectroscopically, and a colourless liquid (4.1 g). Analytical-scale g.l.c. (gas density balance; di-isodecyl phthalate; 78°) indicated that the liquid contained 1,1-dibromotetrafluoroethane (XV) (25% based on the olefin consumed) and (I) (17% recovery); samples of each were isolated by preparative scale g.l.c. and identified spectroscopically.

The involatile reaction mixture was washed with water (400 ml), the insoluble material (4.3 g) was separated, and the aqueous solution was extracted with ether. The extract was dried (MgSO<sub>4</sub>); evaporation under vacuum gave a dark brown oily liquid (2.45 g) which was then distilled under vacuum. The distillate, an orange oil (1.2 g), was shown by comparison of i.r., <sup>19</sup>F n.m.r., and g.l.c. data, to contain *ca.*

a white crystalline solid (0.9 g). Analytical scale g.l.c. showed that the liquid contained (I) (50% recovery) and (XVIII) (7% recovery). The solid, recrystallised from methanol, was shown to be the *dipyridylethane* (XVI) [60% based on (XVIII) consumed], m.p. 91–92° (Found: C, 35.8; F, 56.5%; *M*, 400. C<sub>12</sub>F<sub>12</sub>N<sub>2</sub> requires C, 36.0; F, 57.0%; *M*, 400), λ<sub>max.</sub> (cyclohexane) 280.5 nm (ε 8251), λ<sub>max.</sub> 6.05w, 6.79s, 7.00, 7.78s, 7.96, 8.11s, 8.30s, 9.00w, 9.57w, 10.29, 10.46s, 11.73s, 12.70s, 13.52w, 13.88, 14.16, and 14.33s μm, <sup>19</sup>F δ 78.4 (CF<sub>3</sub>), 90.4 (2-, 6-F), 139.6 (3-, 5-F), and 164.1 p.p.m. (CF) (ratio 3:4:4:1), J<sub>CF,3,5-F</sub> 26, J<sub>CF,3,5-F</sub> 13.5, J<sub>CF,CF,3</sub> 9 Hz.

*Reactions of the Chlorotetrafluoroethylpyridine* (VI).—(a) *With caesium fluoride.* A mixture of caesium fluoride (2.0 g, 13.3 mmol), THTD (20 ml), and compound (VI) (0.95 g, 3.3 mmol) was stirred at 90° for 24 h under dry nitrogen. Removal of the volatile products under vacuum gave the

TABLE 3

Solvent	Temp. (°C)	CF <sub>2</sub> =CFBr recovered (g)	Volatile product (g)	Residue (g)	Yields (%) *		Conversion (%)
					(VIII)	(IX)	
POPD	90	6.0	2.8	1.0	30	9	62
THTD	90	6.0	4.0	0.2	51	18	64

\* Based on C<sub>4</sub>F<sub>4</sub>N<sub>2</sub> consumed.

35% by weight of (XVI) [*ca.* 15% yield based on (I) consumed]. This compound was characterised as described later. The residue, which was insoluble in ether, was dissolved in acetone, then water (50 ml) was added to dissolve caesium fluoride and the acetone was removed under vacuum. An aqueous slurry remained which was washed with ether to leave an orange gum (2.7 g), which was neither water- nor ether-soluble and did not contain any identifiable products.

(b) *With tetrafluoropyridazine* (VII). Reactions were carried out similarly; the results of several experiments are summarised in Table 3. The experiments involved the following quantities: caesium fluoride (3.0 g, 20 mmol), solvent (35 ml), compound (VII) (3.0 g, 19.7 mmol), and bromotrifluoroethylene (16 g, 100 mmol), and a reaction time of 2 h. The products (VIII) and (IX) were identified spectroscopically. When a reaction at 90°, in THTD, was continued for a period of 18 h two additional products were obtained: perfluoro-3,4,5-triethylpyridazine<sup>1</sup> (identified spectroscopically) and a small amount of *perfluorotetraethylpyridazine* (Found: C, 25.8; F, 68.2%; *M*, 552. C<sub>12</sub>F<sub>20</sub>N<sub>2</sub> requires C, 26.1; F, 68.8%; *M*, 552), m.p. 37–38°, λ<sub>max.</sub> (cyclohexane) 260br and 356br nm (ε 743 and 200), λ<sub>max.</sub> 7.51, 7.70s, 8.07s, 8.22s, 8.46s, 8.61s, 8.77s, 8.94s, 9.06s, 9.53s, 9.76s, 13.16w, 13.5, 13.62, and 13.79s μm, <sup>19</sup>F δ 73.2 (3-, 6-CF<sub>3</sub>), 80.8 (4-, 5-CF<sub>3</sub>), 91.2 (3-, 6-CF<sub>2</sub>), and 108.8 p.p.m. (4-, 5-CF<sub>2</sub>) (ratio 3:3:2:2).

*Synthesis of 1,1-Bis-(2,3,5,6-tetrafluoro-4-pyridyl)tetrafluoroethane* (XVI).—Perfluoro-4-vinylpyridine (XVIII)<sup>15</sup> (0.9 g, 4.1 mmol) was added dropwise during 15 min to a stirred mixture of caesium fluoride (0.5 g, 3.3 mmol), THTD (3 ml), and compound (I) (0.9 g, 5.3 mmol) under dry nitrogen at *ca.* 50°. After 45 min volatile products were removed under vacuum, giving a colourless liquid (0.5 g) and

perfluoroethyl compound (II) (0.6 g, 60%), identified spectroscopically.

(b) *With sodium methoxide.* A mixture of compound (VI) (0.5 g, 1.75 mmol), dry methanol (30 ml), and sodium methoxide (1.8 mmol, 1 mol. equiv.) in methanol (42 ml) was stirred at 20° for 4 h, poured into water (300 ml), acidified (dil. hydrochloric acid), and extracted with methylene chloride (4 × 25 ml). The combined extracts were washed with water (2 × 10 ml) and then dried (MgSO<sub>4</sub>). Removal of solvent under vacuum gave 4-(1-chlorotetrafluoroethyl)-2,3,5-trifluoro-6-methoxyppyridine (XIV) (0.45 g, 85%) (Found: C, 32.0; Cl, 11.9; F, 44.2%; *M*, 297, 299. C<sub>8</sub>H<sub>3</sub>ClF<sub>7</sub>N requires C, 32.3; Cl, 11.9; F, 44.7%; *M*, 297, 299), b.p. 192°, λ<sub>max.</sub> (cyclohexane) 301br nm (ε 4265), λ<sub>max.</sub> 3.37w, 6.06w, 6.68s, 6.92s, 7.12, 7.78s, 7.92s, 8.11s, 8.28s, 9.81, 10.08, 10.52, 10.72s, 10.81s, 12.40, 12.57w, 13.91, and 14.55 μm, <sup>19</sup>F δ 83.2 (CF<sub>3</sub>), 93.4 (2-F), 125.3 (CF), 137.2 (5-F) and 150.0 p.p.m. (3-F) (ratio 3:1:1:1:1), <sup>1</sup>H δ 4.1 (OMe).

*Reaction of 1,1-Dichlorodifluoroethylene with Tetrafluoropyridazine* (VII).—A mixture of caesium fluoride (3.0 g, 20 mmol), THTD (25 ml), compound (VII) (3.0 g, 19.7 mmol), and 1,1-dichlorodifluoroethylene (12 g, 90.3 mmol) was stirred at 80° for 2 h. Removal of the volatile material under vacuum, followed by fractionation, gave unchanged olefin (3.2 g) and a colourless liquid (4.6 g) which was analysed by g.l.c. and shown to contain compounds (VII) (1.8 g, 60% recovery), (VIII) (1.45 g, 65%), and (IX) (0.15 g, 5%), identified spectroscopically, together with traces of unidentified material.

We thank the S.R.C. for a Studentship (to M. Y. G.) and Professor W. K. R. Musgrave for his interest.

[3/135 Received, 22nd January, 1973]