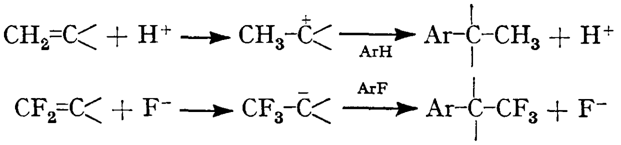
Reactions Involving Fluoride Ion. Part I.[1] The Polyfluoroalkylation of Fluorinated Aromatic Systems

By **R. D. Chambers,*** **J. A. Jackson**, **W. K. R. Musgrave**, and **R. A. Storey**, Chemistry Department, Science Laboratories, South Road, Durham City

Highly fluorinated aromatic compounds and their derivatives will react with carbanions produced from fluorinated olefins and fluoride ion, with the formation of polyfluoroalkyl derivatives, in a process which is the nucleophilic equivalent of the Friedel-Crafts reaction in hydrocarbon chemistry. Reaction occurs between hexafluoropropene and pentafluoropyridine, pentafluoronitrobenzene, and other activated systems like octafluorotoluene, pentafluorobenzonitrile, and methyl pentafluorobenzoate. Polysubstitution is achieved by increase in the pressure of the olefin, and $CF_3CF_2^-$ is a more effective nucleophile than $(CF_3)_2CF^-$. Potassium or caesium fluoride may be used for initiation and, as solvents, tetraglyme and sulpholan are better than dimethylformamide, diglyme, and triglyme.

MUCH information has now accumulated concerning the chemistry of polyfluoro-olefins [2,3] and -aromatic systems; [4-6] the predominant feature of each type is the susceptibility to nucleophilic attack. These fluorocarbons thus exhibit a chemistry complementary to that of the corresponding hydrocarbon systems. Miller and his co-workers [7] first demonstrated that carbanions can be generated by reaction of polyfluoro-olefins with fluoride ion in aprotic solvents, and reactions of these carbanions [8] with, *e.g.*, halogens [9] and acid fluorides [10] lead to fluorocarbon iodides and ketones respectively. Also, Graham and his co-workers [11] have recently reported similar reactions between fluorocarbanions and tetrafluoroethylene, fluoro-ketones, and carbon dioxide. Consequently, these and other reactions have substantiated the analogy between the fluoride ion in fluorocarbon chemistry and the proton in hydrocarbon chemistry. On this basis we have investigated the reactions of polyfluorocarbanions, generated from fluoro-olefins, with polyfluoroaryl systems, in what can be regarded as the nucleophilic equivalent of Friedel-Crafts reactions.



$$CH_2{=}C\!< + H^+ \longrightarrow CH_3{-}\overset{+}{C}\!< \xrightarrow[ArH]{} Ar{-}\underset{|}{\overset{|}{C}}{-}CH_3 + H^+$$

$$CF_2{=}C\!< + F^- \longrightarrow CF_3{-}\overset{-}{C}\!< \xrightarrow{ArF} Ar{-}\underset{|}{\overset{|}{C}}{-}CF_3 + F^-$$

Pentafluoropyridine was chosen as substrate, since it is considerably more susceptible to attack by nucleophiles than hexafluorobenzene.[5,6] Sulpholan was used as solvent, since it is effective for a number of fluorination reactions with potassium fluoride.[12] The reagents were contained in a Carius tube at 120° and gave perfluoro-(4-isopropylpyridine) (I) in high yield, together with only a trace of di-substituted compound (II). The conditions

$$C_5F_5N + CF_3{\cdot}CF{:}CF_2 \xrightarrow[130°,\ 12\ hr]{KF,\ sulpholan} \underset{(I)}{4\text{-}[(CF_3)_2CF]{\cdot}C_5F_4N}\ (94\%) + \underset{(II)}{2,4\text{-}[(CF_3)_2CF]_2{\cdot}C_5F_3N}$$

were varied in order to establish the relative effectiveness of sulpholan, diglyme, triglyme, and dimethylformamide as solvents and of potassium and caesium fluorides as initiators. The results for two series of reactions, one with potassium fluoride in different solvents at 130°, and the other with potassium or caesium fluoride at 20°, are shown in Table 2. Sulpholan is shown to be the most useful solvent for this system, but this result may not apply to others, particularly where different fluoro-olefins are employed. In fact, tetraglyme

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[1] Preliminary communication, R. D. Chambers, R. A. Storey, and W. K. R. Musgrave, *Chem. Comm.*, 1966, 384.

[2] A. Lovelace, W. Postelnek, and D. A. Rausch, 'Aliphatic Fluorine Compounds,' Reinhold, New York, 1958.

[3] R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, 1965, **4**, 50.

[4] J. C. Tatlow, *Endeavour*, 1963, **22**, 89.

[5] R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc.*, 1965, 3736.

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

[7] W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091, and references contained therein.

[8] See references contained in ref. 3.

[9] C. G. Krespan, *J. Org. Chem.*, 1962, **27**, 1813.

[10] F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Amer. Chem. Soc.*, 1962, **84**, 4275; R. D. Smith, F. S. Fawcett, and D. D. Coffman, *ibid.*, p. 4285.

[11] D. P. Graham, *J. Org. Chem.*, 1966, **31**, 955; D. P. Graham and V. Weinmayr, *ibid.*, p. 957; D. P. Graham and W. B. McCormack, *ibid.*, p. 958.

[12] G. Fuller, *J. Chem. Soc.*, 1965, 6264, and references contained therein.

appeared more effective than sulpholan in reactions with octafluorotoluene. Caesium fluoride is the more effective initiator; this agrees with the results of the study of fluorination reactions with alkali-metal fluorides,[13] in which the effectiveness of the fluoride decreases with increase in lattice energy.[14] However, these polyfluoroalkylation reactions occur at least partly in solution, and this highlights the importance of the effect of the gegenion on the nucleophilic strength of fluoride ion; the smaller gegenions apparently have a greater influence (solvation). Correspondingly, reactions in which potassium fluoride was used were unsuccessful in the absence of a solvent, whereas those in which caesium fluoride was used proceeded as expected, although with less efficiency than in the presence of a solvent.

In all of the reactions in Carius tubes under the conditions described, no more than traces of disubstitution occurred. The main reason is that although twice the theoretical amount of olefin needed for monosubstitution was used, almost half of this was consumed in side reactions which produced dimers and trimers of hexafluoropropene. When perfluoro-(4-isopropylpyridine) was heated with more hexafluoropropene and caesium fluoride at a higher temperature the perfluoro(2,4-diisopropyl)pyridine was formed as expected. In some cases there is probably an additional effect due to the decrease in solubility of the product in the solvent with increase in molecular size; high solubility is not of great importance however, since diglyme is a better solvent than sulpholan for perfluoro-(4-isopropylpyridine) but it still does not make poly-alkylation easier. Another minor factor was the surface of the catalyst (see Table 2); larger amounts of catalyst gave slightly better conversions. However, the main reason for monosubstitution was undoubtedly the low concentration of olefin at the site of the reaction; when this was increased by performing the reaction at 150° in a pressure vessel (the pressure rose to *ca.* 30 atm.), 4-, 2,4-bis-, and a mixture of tris(heptafluoroisopropyl) derivatives (apparently 2,4,5- and 2,4,6-isomers are produced) were obtained. Even when the amount of hexafluoropropene was increased so that the pressure reached a maximum of 67 atm., or when enough nitrogen was introduced initially to give a maximum pressure of 100 atm., or when the starting materials were tris(heptafluoroisopropyl)difluoropyridines, no more than a trace of tetrakis(heptafluoroisopropyl(monofluoropyridine was obtained. When tetrafluoroethylene was used instead of hexafluoropropene a mixture of mono- to pentakis-pentafluoroethyl derivatives was obtained. The reaction of the pentafluoroethyl anion at the 3- and 5-positions of pentafluoropyridine, where no reaction occurred with the heptafluoroisopropyl anion, illustrates the expected greater reactivity of the primary anion. Andreades[15] demonstrated the greater stability of a secondary polyfluorocarbanion, $(CF_3)_2\bar{C}F$, than of a primary ion $^-\bar{C}F_2$. The ion $CF_3{\cdot}\bar{C}F_2$ would therefore be expected to be a much more effective nucleophile than $(CF_3)_2\bar{C}F$. Also, the greater steric requirements of the latter would inhibit polysubstitution.

These latter results fit in with a recent report by Imperial Chemical Industries[16] that a mixture of perfluoro-(mono-, di-, tri-, tetra-, penta-, and hexa-ethylbenzenes) is obtained from hexafluorobenzene, tetrafluoroethylene, and potassium fluoride at 135° in 6 hr. at *ca.* 34 atm.

Pentafluoronitrobenzene has been shown[17] to be of similar reactivity towards nucleophiles as pentafluoropyridine and was polyfluoroalkylated, under the conditions indicated, by use of hexafluoropropene. Both mono- (III) and disubstitution (IV) of fluorine occurred; other products (V) arose from displacement of the nitro-group by fluoride ion. This is to be expected, since in other aromatic systems[17,18] nucleophilic displacement of the nitro-group occurs with similar ease to that of fluoride. The reaction conditions appear to be highly critical: when this reaction was performed with use of an autoclave on a larger scale and at a higher temperature, replacement of the nitro-group was much more extensive, and the major product was perfluoro(isopropylbenzene).

$$\begin{aligned} C_6F_5{\cdot}NO_2 + CF_3{\cdot}CF{:}CF_2 &\xrightarrow[\text{12 hr., 120°}]{\text{KF, sulpholan}} \underset{\text{(III)}}{p\text{-}[(CF_3)_2CF]{\cdot}C_6F_4{\cdot}NO_2\ (25\%)} \\ &+ \underset{\text{(IV)}}{op\text{-}[(CF_3)_2CF]_2{\cdot}C_6F_3{\cdot}NO_2\ (20\%)} \\ &+ \underset{\text{(V)}}{m\text{- and } p\text{-}[(CF_3)_2CF]_2{\cdot}C_6F_4} \end{aligned}$$

To study the scope of the reaction, a range of polyfluorobenzenes with various substituents was investigated. Under the mild conditions (Carius tubes) used for mono-substitution in pentafluoropyridine, no reaction of hexafluorobenzene, bromopentafluorobenzene, or 1,3,5-trichlorotrifluorobenzene with hexafluoropropene was detected. Indeed, all efforts so far to cause hexafluoropropene to react with hexafluorobenzene have failed.[19] However, more reactive derivatives such as octafluorotoluene and methyl pentafluorobenzoate gave the expected products, perfluoro-(4-isopropyltoluene) (VI) and methyl perfluoro-(4-isopropylbenzoate) (VII) respectively. The reaction between octafluorotoluene and hexafluoropropene was used to compare the efficiencies of sulpholan and tetraglyme as solvents. With caesium fluoride they were equally effective but with potassium fluoride as initiator tetraglyme gave a con-

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[13] M. Hudlicky, 'Chemistry of Organic Fluorine Compounds,' Pergamon, Oxford, 1961, p. 104.

[14] A. G. Sharpe, *Quart. Rev.*, 1957, **11**, 49.

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

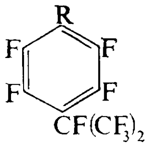
[16] I. C. I. Patent, *Derwent Patent Rev.*, 1966, **48**, abs. no. 681,674.

[17] R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc.* (*B*), 1966, 220.

[18] J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1; J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 273.

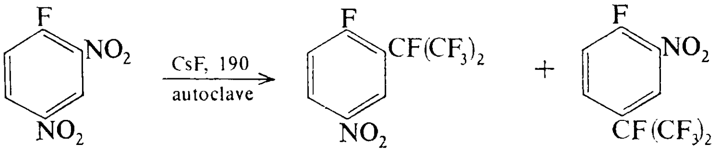
[19] R. L. Dressler and J. A. Young, *J. Org. Chem.*, 1967, **32**, 2004.

siderably higher yield of the product (VI). This indicates that solvation of the caesium cation does not affect the reactivity of fluoride ion very much, but solvation of the potassium cation is very important and is more efficient in tetraglyme.



(VI) R=CF$_3$
(VII) R=CO$_2$Me
(VIII) R=CN
(IX) R=F

Reaction occurred with pentafluorobenzonitrile much more readily than with the other benzene derivatives and could only be controlled at about 20°, when the 4-heptafluoroisopropyl derivative (VIII) was obtained. Higher temperatures gave complex mixtures of polyalkylated products, some containing no nitrogen, and the reaction is being investigated further. The nitrile (VIII) was first hydrolysed to the corresponding amide with conc. sulphuric acid and then to the carboxylic acid with 18N-sulphuric acid. With 2,4-dinitrofluorobenzene, a reactive but not a highly fluorinated substrate, replacement of the nitro-group occurred, as with pentafluoronitrobenzene when the reaction was carried out with use of an autoclave, to give a low yield of the corresponding heptafluoroisopropyl derivatives. Much tar was formed, and polyfluoroalkylation will probably be limited by the fact that fluoride ion is a very strong base in aprotic solvents and will abstract ring hydrogen. In support of this it has been noted previously that attempted replacement of ring chlorine by fluorine often results in decomposition if ring hydrogen is present.

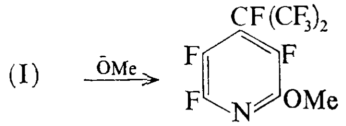


The limiting feature in the use of hexafluoropropene in these polyfluoroalkylation reactions is the tendency for the formation of higher molecular-weight material from the olefin in the presence of alkali-metal fluorides.[20]

Although it was not recorded accurately, variation in the reaction conditions altered the proportion of dimers to trimers formed; low temperature and pressure favoured the dimers. The dimers could not be separated from trimers by distillation but were readily separated by g.l.c. I.r. and n.m.r. examination of the dimer collected from a number of experiments indicated that the principal component was perfluoro-(2-methylpent-2-ene) (X); a little perfluoro-(4-methylpent-2-ene) (XI) was also obtained. The formation of these can easily be accounted for in terms of self-condensation of the olefin, followed by fluoride-ion initiated rearrangements. The trimer was a mixture of three components which could only be partially resolved by g.l.c.

$$\begin{tikzcd}
F^- + CF_2{:}CF{\cdot}CF_3 \arrow[r] & (CF_3)_2\bar{C}F + CF_2{:}CF{\cdot}CF_3 \arrow[d] \\
(CF_3)_2CF{\cdot}CF{:}CF{\cdot}CF_3 \ \text{(XI)} \arrow[d, "F^-"] & {[(CF_3)_2CF{\cdot}CF_2{\cdot}CF{\cdot}CF_3]} \arrow[l, "-F^-"'] \\
{[(CF_3)_2CF{\cdot}CF{\cdot}CF_2{\cdot}CF_3]} \arrow[r, "-F^-"] & (CF_3)_2C{:}CF{\cdot}CF_2{\cdot}CF_3 \ \text{(X)}
\end{tikzcd}$$

The orientation of polyfluoroalkylation was determined from n.m.r. measurements (see Table 1) and, in the pyridine series, from the known orientation of attack by other nucleophiles. Monosubstitution in pentafluoropyridine is known to occur exclusively in the 4-position;[5,6] this was confirmed by the fluorine-19 spectrum of perfluoro-(4-isopropylpyridine), which showed only two absorptions from ring fluorine (Table 1). This was also indicated by a large (40 c./sec.) coupling between the tertiary fluorine and the 3- and 5-fluorines and by a smaller coupling (10 c./sec.) between CF_3 and the latter fluorine atoms. The position of entry of the second heptafluoroisopropyl group could not be assigned directly from the n.m.r. spectrum of the disubstituted compound. While a second nucleophilic group usually enters at the 2-position, the *ortho*-activating influence of a polyfluoroalkyl group could be significant. The position of entry of a methoxy-group could, however, be determined; this occurred exclusively in the 2-position (XII). Therefore, a second heptafluoroisopropyl group must enter at this position since entry *ortho* to the 4-substituent would be even less likely than with a methoxy-group, for steric reasons. The fluorine-19 chemical shifts which arise from introduction of a methoxy-group at C-2 have been previously determined;[17] with perfluoro-(4-isopropylpyridine) as reference, the calculated and observed shifts, as shown below, are in close agreement.



(XII)

Chemical shifts for ring fluorine in (XII)

	3-	5-	6-
Observed	−28·0	−15·8	−71·4
Calc..................	−27·8	−16·8	−71·6

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[20] W. J. Brehm, K. G. Bremer, H. S. Eleuterio, and R. W. Meschke, U.S.P. 2,918,501/1959 (*Chem. Abs.*, 1960, **54**, 20,875).

TABLE 1

Fluorine-19 n.m.r. data

	Chemical shift * in p.p.m. (J in c./sec.)	Assignment
(I)	−75·6	2,6-F
	−27·8	3,5-F
	−88·6 ($J_{3,5F}$ 14)	$\text{4-CF(C}F_3)_2$
	+15·6 ($J_{3,5F}$ 45)	$\text{4-C}F(\text{CF}_3)_2$
(II)	−81	6-F
	(−50·6; −40·2)	(3- or 5-F)
	−89·0	$\text{2- and 4-CF(C}F_3)_2$
	+14·8	$\text{4-C}F(\text{CF}_3)_2$
	+19·5	$\text{2-C}F(\text{CF}_3)_2$
(XII)	−71·4	6-F
	−15·8	5-F
	−28·0	3-F
	−88	$\text{4-CF(C}F_3)_2$
	+15·0	$\text{4-C}F(\text{CF}_3)_2$
(VI)	(−26·5; −32·4)	(2,6- and 3,5-F)
	−107	$\text{–C}F_3$
	−90	$\text{–CF(C}F_3)_2$
	+14·7	$\text{–C}F(\text{CF}_3)_2$
(III)	(−18·3; −31)	(2,6- and 3,5-F)
	−89 ($J_{\text{CF}_3,\text{F}}$ 5)	$\text{–CF(C}F_3)_2$
	+14·7 ($J_{2,6F}$ 13)	$\text{–C}F(\text{CF}_3)_2$
(IV)	−90 (dd)	$\text{2-CF(C}F_3)_2$
	−88 (dt)	$\text{4-CF(C}F_3)_2$
(IX)	−80	$\text{–CF(C}F_3)_2$
	−18	(2- and 6-F)
	−5	4-F
	+8	(3- and 5-F)
	+26	$\text{–C}F(\text{CF}_3)_2$
Perfluoro-(4-ethylpyridine)	−79	$\text{–CF}_2\text{C}F_3$
	−25	$\text{–C}F_2\text{CF}_3$
	−51	3,5-F
	−76	2,6-F

* From C_6F_6 as internal standard.

EXPERIMENTAL

Purification of Reagents.—Potassium and caesium fluorides were reagent grade, dried by heating in a nickel beaker over a bunsen burner for several hr., and then stored at 150° until required. The sulpholan was dried and repeatedly distilled under vacuum until the distillate readily solidified. Dimethylformamide (DMF) was repeatedly distilled. Diglyme, triglyme, and tetraglyme were dried by distillation from sodium under vacuum.

Reaction of Pentafluoropyridine with Hexafluoropropene.—(a) *With potassium fluoride in sulpholan.* Pentafluoropyridine (3·0 g., 17·8 mmoles), anhydrous potassium fluoride (3·0 g., 55·9 mmoles), and sulpholan (15 ml.) were introduced into a Carius tube (*ca.* 100 ml.) and hexafluoropropene (5·0 g., 33·3 mmoles) was introduced from a vacuum system. The tube was sealed under vacuum and heated for 12 hr. at 130°. It was then cooled in liquid air and opened to a vacuum system. The volatile components were fractionated in the vacuum system to give hexafluoropropene (0·5 g.), and higher boiling material (8 g.). The latter was separated by g.l.c. (silicone elastomer on Celite) to give (i) derivatives of hexafluoropropene (2·7 g.), (ii) pentafluoropyridine (0·3 g.), (iii) *perfluoro-(4-isopropylpyridine)* (4·8 g., 94%) (Found: C, 29·9; F, 65·0%; *M*, 319. $C_8F_{11}N$ requires C, 30·1; F, 65·5%; *M*, 319), b.p. 128—129°, and (iv) *perfluoro-(2,4-di-isopropylpyridine)* (0·2 g.) (Found: C, 27·8%; *M*, 469. $C_{11}F_{17}N$ requires C, 28·1%; *M*, 469).

(b) *With various solvent–initiator systems.* The procedure described in (a) was repeated with either potassium fluoride or caesium fluoride (3 g. or 8 g.) as initiator, and sulpholan, diglyme, triglyme, or dimethylformamide as solvent. In reactions in which the initial temperature was 20° the sealed tubes were shaken vigorously without external heating on a Vibroshaker for 12 hr. The products were isolated as in (a) and the results are shown in Table 2.

(c) *With potassium fluoride and no solvent.* The procedure described in (a) was repeated. Hexafluoropropene (4·3 g.) and pentafluoropyridine (2·9 g.) were recovered.

(d) *With caesium fluoride and no solvent.* The experiment was repeated as in (a) but without solvent and with caesium fluoride (3·0 g., 19·7 mmoles) instead of potassium fluoride. The products were (i) derivatives of hexafluoropropene (2·95 g.), (ii) pentafluoropyridine (0·69 g.), and (iii) perfluoro-(4-isopropylpyridine) (4·4 g., 99% based on perfluoropyridine consumed).

Reaction of Perfluoro-(4-isopropylpyridine) with Sodium Methoxide.—To a stirred solution of perfluoro-(4-isopropylpyridine), 2·512 g., 7·847 mmoles) in methanol (20 ml.), was added a solution of sodium (0·168 g.) in methanol (20 ml.) during 15 min. at room temperature. The mixture was stirred for a further 30 min., heated under reflux for 1 hr., then poured into water. The mixture was extracted with methylene dichloride. The combined extracts were dried ($MgSO_4$), and the solvent was distilled off to leave a pale yellow oil. Distillation of this oil gave *4-heptafluoroisopropyl-2-methoxy-3,5,6-trifluoropyridine* (2·1 g., 80%), b.p. 170°/760 mm. (Found: C, 32·9; H, 0·95. $C_9H_3F_{10}NO$ requires C, 32·6; H, 0·90%). Its structure was shown by its ^{19}F n.m.r. spectrum.

Reaction of Perfluoro-(4-isopropylpyridine) with Hexafluoropropene in the Presence of Caesium Fluoride in Sul-

TABLE 2

Reaction between perfluoropyridine (3·0 g., 17·75 mmoles) and hexafluoropropene (5·0 g., 33·3 mmoles)

Initiator/solvent	Temp.	Total yield (g.)	Monosubstituted product (g.)	Perfluoropyridine recovered (g.)	Conversion of perfluoropyridine (%)	Yield (%, based on consumed perfluoropyridine)	Olefin dimers etc. (g.)
KF/diglyme	130°	5·0	1·3	2·0	33	69	1·7
KF/triglyme	130	6·3	2·7	1·5	50	95	2·1
KF/DMF	130	6·0	2·4	1·38	54	79	2·18
KF/sulpholan	130	8·0	4·8	0·32	89	95	2·88
KF/diglyme	20	4·5	0·23	2·73	9	45	1·5
KF/sulpholan	20	6·5	3·38	1·1	63	94	2·52
CsF/diglyme	20	6·0	1·9	1·8	40	84	2·3
CsF (8·0 g.) diglyme ...	20	6·5	2·0	1·74	42	84	2·26
CsF/sulpholan	20	7·3	4·7	0·37	88	95	2·9
CsF (8·0 g.) sulpholan ...	20	8·5	5·61	0·07	98	100	2·82

All reactions in Carius tubes (100 ml.) with solvent (15 ml.). All reactions at 20° were shaken. Except where stated, quantity of fluoride was 3·0 g. Losses in mass-balance can be attributed to unchanged hexafluoropropene and tar formation.

pholan.—Hexafluoropropene (6·0 g., 40·0 mmoles) was condensed into perfluoro-(4-isopropylpyridine) (3·0 g., 9·40 mmoles), anhydrous caesium fluoride (3·0 g., 19·70 mmoles), and sulpholan (15 ml.) in a Carius tube (100 ml.). The tube was evacuated, sealed, heated at 200° for 20 hr., and cooled. It was opened into a vacuum system, and the volatile components (6·3 g.) were collected by vacuum transfer. Analytical scale g.l.c. (silicone elastomer on Celite) showed that the product was a mixture of derivatives of hexafluoropropene (3·6 g.), perfluoro-(4-isopropylpyridine) (1·2 g.), and perfluoro-(2,4-di-isopropylpyridine) (1·5 g., 54% based on starting material which had reacted).

Reaction of Pentafluoropyridine with Hexafluoropropene at Higher Pressure.—(*a*) Hexafluoropropene (16 g., 100 mmoles) was condensed into pentafluoropyridine (4·0 g., 23·66 mmoles), anhydrous potassium fluoride (3·0 g., 50·8 mmoles), and sulpholan (15 ml.) in a rocking autoclave (50 ml.). The autoclave was evacuated, closed, and heated at 150° for 17 hr. The pressure rose to about 500 lb./in.^{2}, and then fell to about 50 lb./in.^{2} The autoclave was cooled to room temperature and vented, and the contents were washed out with water. The mixture was extracted with ether and the combined extracts were washed with water and dried ($MgSO_4$). Most of the solvent and hexafluoropropene derivatives were distilled off. G.l.c. (di-n-decylphthalate on Celite at 100°) showed the liquid residue (7·3 g.) to consist of ether (1·8 g.), perfluoro-(4-isopropylpyridine) (1·9 g., 25%), perfluoro-(2,4-di-isopropylpyridine) (1·7 g., 14%), and *perfluoro(tri-isopropylpyridine)* (1·9 g., 13%) (Found: C, 27·15%; M, 619. $C_{14}F_{24}N$ requires C, 27·3%; *M*, 619), b.p. 190—192°. The n.m.r. spectrum suggests that this is a **3** : 1 mixture of the 2,4,5- and 2,4,6-isomers.

(*b*) Reaction (*a*) was repeated with C_3F_6 (30 g., 200 mmoles), potassium fluoride (9·4 g.), pentafluoropyridine (5·0 g., 29·6 mmoles), and sulpholan (75 ml.) in a rocking autoclave (150 ml.). The mixture was heated at 190° for 12 hrs.; the pressure reached a maximum of *ca.* 1000 lb./in.^{2} and then fell to 600 lb./in.^{2} after 30 min. The autoclave was cooled to room temperature and vented, and the contents were poured into a round-bottomed flask; all the products were distilled out of the solvent under vacuum. This distillate (32 g.) was fractionated at atmospheric pressure to give (i) hexafluoropropene (trace), (ii) hexafluoropropene derivatives (24·2 g.), b.p. 20°—115°, and (iii) perfluoro(alkylpyridines) (7·8 g.), b.p. 115—190°. G.l.c. (di-n-decyl phthalate on Celite at 100°) showed fraction (iii) to consist of perfluoro-(4-isopropylpyridine) (4·0 g.), perfluoro-(2,4-di-isopropylpyridine) (2·9 g.), and perfluoro-(tri-isopropylpyridine) (0·9 g.).

(*c*) Reaction (*b*) was repeated with hexafluoropropene (37 g., 250 mmoles), caesium fluoride (4·6 g.), pentafluoropyridine (5·0 g., 29·6 mmoles), in tetraglyme (90 ml.). The autoclave was heated to 150° for 12 hr.; the maximum and minimum pressures were approximately the same as in (*b*). The products (40 g.) were worked up as before to give hexafluoropropene derivatives (34·4 g.) and perfluoro(alkyl pyridines) (5·6 g.). The latter consisted of perfluoro-(4-isopropylpyridine) (2·2 g.), perfluoro-(di-isopropylpyridine) (2·5 g.), and perfluoro-(tri-isopropylpyridine) (0·9 g.).

(*d*) Reaction (*b*) was repeated with hexafluoropropene (50 g., 333 mmoles), caesium fluoride (3·0 g.), and a mixture (1 : 4) of perfluoro(di-isopropylpyridine) and perfluoro(tri-isopropylpyridine) (5·1 g.) in sulpholan (20 ml.) in a rocking autoclave (50 ml.). The mixture was heated to 200° for 24 hr.; the maximum and minimum pressures were approximately the same as in (*b*). The products (52 g.) were worked up as before to give hexafluoropropene derivatives (48 g.) and perfluoro(alkyl pyridines) (4·0 g.). The latter consisted of perfluoro(di-isopropylpyridine (0·2 g.) and perfluoro(tri-isopropylpyridine) (3·8 g.). Mass spectrometry indicated a trace of perfluoro(tetraisopropylpyridine) (*M*, 769) in the last fraction.

(*e*) Reaction (*d*) was repeated with hexafluoropropene (45 g.), caesium fluoride (3·0 g.), perfluoro(tri-isopropylpyridine) (4·0 g.), and sulpholan (20 ml.), but in this case nitrogen was introduced into the autoclave so that the initial pressure, at liquid air temperature was 500 lb./in.^{2} The maximum and final pressures were *ca.* 1500 and 1000 lb./in.^{2} respectively. The products (40 g.) consisted of hexafluoropropene polymers (37 g.) and perfluoro(tri-isopropylpyridine (3·0 g.). Mass spectrometry indicated a trace of perfluoro(tetraisopropylpyridine) in the latter.

Reaction between Pentafluoropyridine and Tetrafluoroethylene.—To pentafluoropyridine (10·0 g., 59·3 mmoles), caesium fluoride (3·0 g., 19·5 mmoles), and sulpholan (80 ml.) in a rocking autoclave (150 ml.), cooled in liquid air and evacuated, was added tetrafluoroethylene (60·8 g., 0·6 mole). The autoclave was heated to 170°; after 30 min. the pressure had risen to 2,600 lb./in.^{2}; it fell to 600 lb./in.^{2} during the next 2 hr. After a total of 24 hr. the autoclave was cooled to room temperature and vented through a liquid air trap in which tetrafluoroethylene (38 g.) was collected. The residue in the autoclave was poured into water (400 ml.) and the whole was extracted with ether (4 × 30 ml.). The extracts were dried ($MgSO_4$), the ether was distilled off, and the residue (30 g.) was fractionated to give (i) a liquid b.p. up to 140°/1 atm. (5 g.), (ii) a liquid b.p. 70—100°/0·001 mm. (10 g.), (iii) a liquid b.p. 100—200°/0·001 mm. (10 g.), and a tarry residue (*ca.* 5 g.). All three fractions of the distillate consisted of the same six-component mixture with varying proportions of constituents (large scale g.l.c.; di-n-decyl phthalate or silicone elastomer on Celite at temperatures between 100 and 250°) which could not be separated with the apparatus available. The first component was shown from its retention time to be pentafluoropyridine and repeated injection and elution allowed isolation of the last two components in small quantities. They were shown to be *perfluoro(pentaethylpyridine)* (Found: F, 71·6%; *M*, 669. $C_{15}F_{25}N$ requires F, 71·1%; *M*, 669), m.p. 77—78°, and *perfluoro(tetrafluoroethylpyridine)* (Found: *M*, 569. $C_{13}F_{21}N$ requires *M*, 569). If the other components are assumed to be the mono-, di-, and tri-substituted fluoropyridines, g.l.c. shows the yields to be: perfluoro(ethylpyridine) 30%, perfluoro(diethylpyridine) 21%, perfluoro(triethylpyridine) 21%, perfluoro(tetraethylpyridine) 11%, and perfluoro(pentaethylpyridine) 6%.

Reaction of Octafluorotoluene with Hexafluoropropene.—(a) *With caesium fluoride and tetraglyme at low temperature.* Hexafluoropropene (13·0 g., 86·7 mmoles) was condensed into octafluorotoluene (7·5 g., 31·8 mmoles), caesium fluoride (6·8 g., 42·7 mmoles), and tetraglyme (30 ml.) in a Carius tube (90 ml.). The tube was sealed under vacuum and shaken for 13 hr.; a temperature maximum of *ca.* 40° was reached during the first few hr. owing to the heat of reaction. The tube was cooled in liquid air and opened, and the volatile contents (17·7 g.) were distilled off up to 70°/0·001 mm. The product was separated by preparative scale g.l.c. (di-n-decyl phthalate on Celite at 130°) to give (i) polymers of hexafluoropropene (10 g.), (ii) octafluorotoluene (5·9 g.), and (iii) *perfluoro-(4-isopropyltoluene)* (1·8 g., 59% based on 15% of octafluorotoluene reacted) (Found: C, 31·0; F, 68·4. $C_{10}F_{14}$ requires C, 31·0; F, 68·9%), b.p. 150°.

(b) *With caesium or potassium fluoride in sulpholan or tetraglyme.* Experiment (a) was repeated four times with Carius tubes (100 ml.) containing octafluorotoluene (4·6 g., 19·4 mmoles) and hexafluoropropene (8·0 g., 53·3 mmoles) together with either potassium fluoride (5·0 g., 86·7 mmoles) or caesium fluoride (6·8 g., 42·7 mmoles) and either sulpholan (20 ml.) or tetraglyme (20 ml.). The tubes were heated to 175° for 20 hr., the products were removed as in (a), and the compositions of the distillates determined by g.l.c. (see Table 3).

2,4-di-*isopropyl-1-nitrobenzene*) (1·9 g., 20%), a crystalline solid, m.p. 76—77° (from methanol–water) (Found: C, 28·3%; *M*, 513. $C_{12}F_{17}NO_2$ requires C, 28·0%; *M*, 513).

(*b*) Hexafluoropropene (24·0 g., 160·0 mmoles) was condensed into pentafluoronitrobenzene (21 g., 98·60 mmoles), anhydrous potassium fluoride (20 g., 344·8 mmoles), and sulpholan (70 ml.) in a rocking autoclave. The autoclave was heated at 150° for 13 hr. and cooled, and the contents were worked up as above to give a mixture (28 g.) which was separated as before into (i) perfluoro(isopropylbenzene) (14·1 g.), b.p. 128° (Found: C, 31·8. C_9F_{12} requires C, 32·1%), (ii) perfluoro-(1,3- and 1,4-di-isopropylbenzenes) (6·8 g.), and (iii) pentafluoronitrobenzene (6·8 g.).

TABLE 3

Comparison between sulpholan and tetraglyme as solvents for polyfluoroalkylation of octafluorotoluene

Initiator/solvent	Total product (g.)	Hexafluoropropene polymers (g.)	Octafluorotoluene		Wt. of product (g.)	Yield (based on octafluorotoluene consumed) (%)
			Recovered (g.)	Reacted (%)		
KF/sulpholan	11·6	7·3	2·5	45·6	1·8	49·9
KF/tetraglyme	11·8	6·9	1·6	63·1	3·3	64·0
CsF/sulpholan	9·9	4·8	2·5	45·7	2·6	71·9
CsF/tetraglyme	9·8	4·6	1·5	66·3	3·7	69·4

Octafluorotoluene (4·6 g.), hexafluoropropene (8·0 g.), and solvent (20 ml.), in Carius tubes (100 ml.) were used in all experiments.

Reaction of Methyl Pentafluorobenzoate with Hexafluoropropene.—Hexafluoropropene (5·0 g., 33·3 mmoles) was condensed into methyl pentafluorobenzoate (3·9 g., 17·25 mmoles), anhydrous potassium fluoride (3·0 g., 50·8 mmoles), and sulpholan (15 ml.) in a Carius tube (100 ml.). The tube was sealed under vacuum and heated at 140° for 12 hr. The contents were then washed out with water. The mixture was extracted with ether and the combined extracts were washed well with water and dried ($MgSO_4$). The solvent was then distilled off. The residue (5·5 g.) was separated by g.l.c. (silicone elastomer on Celite) into low-boiling olefin derivatives (1·2 g.), methyl pentafluorobenzoate (2·4 g.), and *methyl perfluoro-(4-isopropylbenzoate)* (1·8 g.), b.p. 42°/1·0 mm. (Found: C, 35·4; H, 0·85; F, 55·6. $C_{11}H_3F_{11}O_2$ requires C, 35·1; H, 0·80; F, 55·6%).

Reaction of Pentafluoronitrobenzene with Hexafluoropropene.—(*a*) Hexafluoropropene (4·5 g., 30·0 mmoles) was condensed into pentafluoronitrobenzene (4·2 g., 20·48 mmoles), anhydrous potassium fluoride (4·0 g., 74·57 mmoles), and sulpholan (15 ml.) in a Carius tube (100 ml.). The tube was sealed under vacuum, heated for 12 hr. at 120°, cooled in liquid air, and opened to a vacuum system. The volatile components consisted of a blue gas (which quickly turned brown when exposed to the air), which was not identified but is evidently an oxide of nitrogen, and a trace of hexafluoropropene (i.r. spectroscopy). The residual sulpholan solution was added to water and extracted with ether (3 × 20 ml.); the combined extracts were repeatedly washed with water and dried ($MgSO_4$), and the solvent was distilled off. The products (6·2 g.) were separated by preparative scale g.l.c. (silicone elastomer on Celite at 100°) to give (i) a liquid (2·5 g.) shown by ^{19}F n.m.r. spectroscopy to be a 1 : 1 mixture of perfluoro-(1,3-di-isopropylbenzene) and perfluoro-(1,4-di-isopropylbenzene) which could not be separated because of the identical retention times, (ii) 4-*heptafluoroisopropyl-1-nitrotetrafluorobenzene* (1·8 g., 25%), a yellow liquid, b.p. 189—190° (Found: C, 29·2%; *M*, 363. $C_9F_{11}NO_2$ requires C, 29·7%; *M*, 363), and (iii) *perfluoro-*

Reaction of Pentafluorobenzonitrile with Hexafluoropropene—Hexafluoropropene (4·5 g., 30·0 mmoles) was condensed into pentafluorobenzonitrile (6·5 g., 33·6 mmoles), potassium fluoride (3·0 g., 55·9 mmoles), and sulpholan (15 ml.) in a Carius tube (100 ml.) at liquid air temperature. The tube was sealed under vacuum, heated at 125° for 15 hr., then cooled. The contents were washed out with water and the mixture was extracted with ether (3 × 15 ml.). The combined extracts were washed with water and dried ($MgSO_4$), and most of the solvent was distilled off to leave a pale yellow liquid (7·3 g.). The product was separated by preparative scale g.l.c. (silicon elastomer at 100°) into (i) ether (1·7 g.), (ii) pentafluorobenzonitrile (3·3 g.), (iii) perfluoro-(4-isopropylbenzonitrile) (1·8 g., 30% based on pentafluorobenzonitrile reacted) (Found: C, 34·5. $C_{10}F_{11}N$ requires C, 35·0%), b.p. 191—192°, and (iv) more highly alkylated products (0·5 g.).

Hydrolysis of Perfluoro-(4-isopropylbenzonitrile).[21]—The nitrile (5 g.) was heated to 100° with stirring with conc. sulphuric acid (8 ml.) for 90 min. The mixture was cooled and poured into a large excess of ice–water and the white solid which separated was extracted with ether (3 × 20 ml.). The extract was dried ($MgSO_4$) and the ether distilled off to leave a white solid (5 g.); this gave 4-*heptafluoroisopropyltetrafluorobenzamide* (4 g., 69%), m.p. 71° (from ethanol) (Found: C, 32·9; H, 0·6; F, 57·6; N, 3·6%; *M*, 361. $C_{10}H_2F_{11}NO$ requires C, 33·2; H, 0·55; F, 57·8; N, 3·9%; *M*, 361).

Hydrolysis of 4-Heptafluoroisopropyltetrafluorobenzamide.[23]—The amide (4 g.) and 18N-sulphuric acid (10 ml.) were heated under reflux for 7 hr. The mixture was cooled and poured into a large excess of ice–water from which the acid was extracted with ether (3 × 20 ml.). The extract was dried ($MgSO_4$) and the ether distilled off to leave a white solid which was sublimed to give pure 4-*heptafluoroisopropyltetrafluorobenzoic acid* (3 g., 80%), m.p. 95° (Found: C, 32·7; H, 0·3; F, 56·9%; *M*, 362. $C_{10}HF_{11}O_2$ requires C, 33·15; H, 0·3; F, 57·7%; *M*, 362).

Composition of Mixture of Derivatives of Hexafluoropropene.—The polymeric products (2·0 g.) from several experi-

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[21] Method from L. Belf, Imperial Smelting Corpn. Ltd., private communication.

ments were combined and separated by preparative scale g.l.c. (di-n-decyl phthalate at 80°) to give (i) a dimer (9·2 g., 46%) and (ii) a mixture of three trimers (10·8 g., 54%). The dimer still showed as a single peak on the same g.l.c. column at 25° (Found: C, 23·9; F, 76·3%; *M*, 300. Calc. for C_6F_{12}: C, 24·0; F, 76·0%; *M*, 300). The mass spectrum showed fragments with *m/e* 281 (C_6F_{11}), 231 (C_5F_9), 212 (C_5F_8), 181 (C_4F_7), 143 (C_4F_5), 131 (C_3F_5), 93 (C_2F_3), and 69 (CF_3); and the double bond absorbed in the i.r. at 5·92 μ. A compound characterised as $(CF_3)_2{\cdot}C{:}CF{\cdot}CF_2{\cdot}CF_3$ was obtained previously in this laboratory from the reaction between hexafluoropropene and trimethylamine [22] (in which fluoride ion is produced). The fluorine-19 chemical shifts from trifluoroacetic acid (external reference) for this compound are (relative intensities in brackets) −23·5 (3) and −21·0 (3) [$(CF_3)_2C{:}C$], +2·1 (3) ($CF_3{\cdot}C{\cdot}$), +16·5 (1) (${\cdot}CF{:}$), and +35·4 (2) (${\cdot}CF_2{\cdot}$) p.p.m. Comparison of the infrared and n.m.r. spectra of the dimer with the corresponding data for $(CF_3)_2C{:}CF{\cdot}CF_2{\cdot}CF_3$ indicates that the dimer consists principally of this compound, with a small amount of another component, probably $(CF_3)_2CF{\cdot}CF{:}CF{\cdot}CF_3$. The n.m.r. data given above is partly at variance with corresponding data given by Dresdner and co-workers [23] for $(CF_3)_2C{:}CF{\cdot}CF_2{\cdot}CF_3$; perhaps an error in assignment by the latter together with different referencing conditions could account for the difference. The mixture of trimers could not be separated on the columns available but two fractions obtained by partial separation both showed a molecular ion in the mass spectrum at 450 and the same elemental analyses (Found: C, 23·9; F, 76·1, and C, 23·9; F, 75·4, respectively. Calc. for C_9F_{18}: C, 24·0; F, 76·0%).

Reaction of 2,4-*Dinitrofluorobenzene with Hexafluoropropene*.—Hexafluoropropene (9·5 g., 15·8 mmoles) was introduced into an evacuated autoclave (35 ml.) containing 2,4-dinitrofluorobenzene (2·0 g., 10·7 mmoles), caesium fluoride (2·0 g., 13·3 mmoles), and sulpholan (20 ml.) cooled in liquid air. The autoclave was sealed, shaken at 190° for 16 hr., and left to cool; when it was vented, no hexafluoropropene was recovered. The contents were poured into water (300 ml.); the presence of tarry material indicated that considerable decomposition had taken place. The mixture was continuously extracted with benzene for 24 hr. and washed with water. The benzene layer yielded a deep red liquid (2·0 g.). This was distilled under vacuum; analytical scale g.l.c. (180°) indicated that the distillate contained mainly two components of similar retention time. These components were isolated by preparative scale g.l.c. and shown to be a mixture of 2-*heptafluoroisopropyl*-4-*nitro*- and 4-*heptafluoroisopropyl*-2-*nitro-fluorobenzene* (Found: C, 34·7; F, 48·7. $C_9H_3F_8NO_2$ requires C, 34·9; F, 49·2%), M^+ (mass-spectrum) 309, fragmentation pattern consistent with the assignment. The ^{19}F n.m.r. spectrum showed absorptions at +20·4 and +13·4 [$-CF-(CF_3)_2$], −60·4 (two coincident ring fluorine signals), and −87·6 and −88·0 [$-CF-(CF_3)_2$] p.p.m. (from C_6F_6).

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