# Perfluorocarbon fluids as solvent replacements

Richard D. Chambers * and Andrew R. Edwards

*Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham,
UK DH1 3LE*

Perfluoroperhydrophenanthrene 1 may be used as a 'bulking agent' to minimise the problem of solvent
recovery in halogen exchange ('Halex') reactions for the preparation of octafluorocyclopentene 8, and
chlorofluoro-pyridine, -pyrimidine and -benzene derivatives. New 'one-pot' procedures for the syntheses
of hexafluorobut-2-yne 3, octafluorobut-2-ene 11 and hexafluorocyclobutene 7 are described.

Introduction

Saturated perfluorocarbons (PFCs), *e.g.* perfluoroperhydro-phenanthrene **1**, are now industrially available over a wide
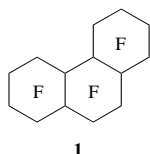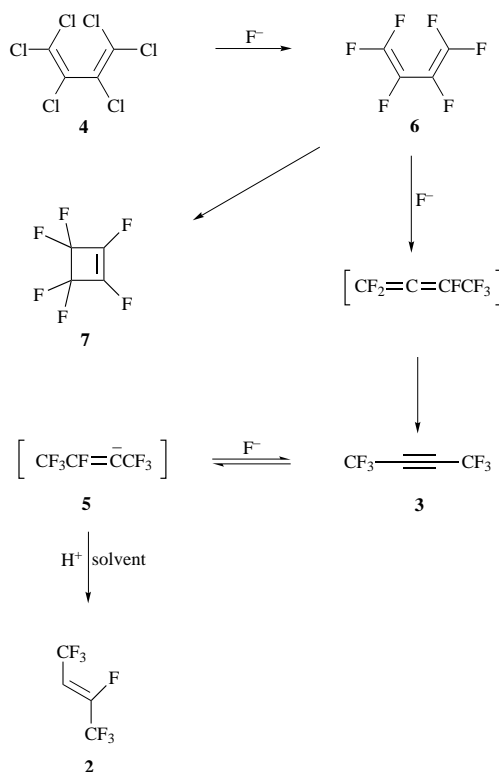

boiling-point range. They are essentially chemically inert, with exceptions including defluorinations over hot metal[1] and the interesting direct reaction with thiophenate,[2] and are generally regarded as largely immiscible with most organic solvents, although published data is sparse. Miscibility with $CFCl_2CF_2Cl$ and some low molecular weight hydrocarbons is recorded, together with the fascinating solubility of gases such as oxygen, carbon dioxide and chlorine.[3]

It is our view that there is considerable potential for use of PFCs as 'bulking agents' in chemistry, where solvent is reduced significantly by replacement with a PFC which can be recovered simply by separation (possibly with cooling) and recycled without purification at the end of the reaction. In addition to reduced solvent consumption and/or disposal problems, there is the added benefit that the use of a PFC would lead to reduced explosion hazards. So far, the potential general benefits of PFCs do not appear to have been recognised and, in this paper, we demonstrate that PFCs may be used effectively in the so-called 'Halex' process for exchange of chlorine by fluorine, using potassium fluoride. This process is operated on the industrial scale for a number of products and solvent recovery can pose waste disposal problems. Furthermore, established procedures have proven hazardous.[4]

Results and discussion

We have a continued interest in the chemistry of 2*H*-hepta-fluorobut-2-ene **2**† and hexafluorobut-2-yne[5–7] **3**; a synthesis of **2** has been described by Maynard[8] and, also, interesting by-products have been revealed in more recent investigations.[9] Overall, the reaction involves exchange of chlorine in hexa-chlorobutadiene **4** by fluorine (Scheme 1) using potassium fluoride in an aprotic solvent. In the present series of investigations sulfolane, *i.e.* tetrahydrothiophene 1,1-dioxide (THTD), has been used as the solvent, and it is curious that the proton

---

† For clarity, the names of compounds of this type show the positions of the hydrogen atoms (indicated hydrogens). The IUPAC name for this compound is 1,1,1,2,4,4,4-heptafluorobut-2-ene.
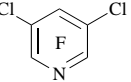
Scheme 1 Reaction sequence for the synthesis of hexafluorocyclo-butene **7**, hexafluorobut-2-yne **3** and 2*H*-heptafluorobut-2-ene **2**

in **2** is most likely originating from the solvent in the final step of the process **3** to **2**, *via* **5**, although prior to this work, the mechanism of formation of **2** had not been firmly established.

We have used this halogen exchange system and addressed the question of what proportion of the THTD may be replaced by a perfluorocarbon. Perfluoroperhydrophenanthrene **1**, bp 215 °C, wa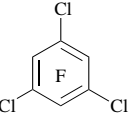s selected as a suitable solvent replacement because of its high boiling point and we found that the reaction proceeded efficiently when up to 75% v/v of the solvent normally required,[8] had been replaced by the equivalent volume of **1**. However, no reaction occurred when only 10% of the normal THTD charge was used. Nevertheless, when replacing up to 75% of the normal THTD charge, reactions were carried out efficiently using either a Carius tube, or atmospheric pressure conditions on a larger scale. What is remarkable, however, is that the observed product contained *ca.* 75% of hexafluorobut-2-yne **3** and 25% of **2**. We are unaware of any previous report of the direct synthesis of **3** from **4** and these observations, coupled with the recent finding that dehydrofluorination of **2** to the butyne **3** occurs on standing the former over molecular sieves,[6]

Table 1 Fluorination of chlorocarbons using KF and 25% v/v of THTD

Chlorocarbon	THTD[a] (%)	CT[b]/AP[c]	Products	Yield (%)
4	25	AP	**3**	56[d]
	10	AP	No reaction	—
	KF coated[e]	AP	No reaction	—
	25	CT	**2**	60
(chlorocyclopentene)	25	AP	(fluorocyclopentene) **8**	58
	25	CT	(fluorocyclopentene) **8**	89
	0	CT	No reaction	—
(chloropyridine)	25	AP	(3,5-dichloro-4-fluoropyridine)	93
	25	CT	,,	59
	0	CT	No reaction	—
(chloropyrimidine)	25	CT	(chlorofluoropyrimidine)	71
(chlorobenzene)	25	CT	(trichlorofluorobenzene)	83

[a] Volume %. [b] Carius tube. [c] Atmospheric pressure. [d] % After leaving over molecular sieves for 25 days.[6] [e] The potassium fluoride used had been soaked in THTD and the excess solvent decanted off.

Table 2 Fluorination of aromatic compounds using KF, perfluorocarbon and 18-crown-6 **9**

Chlorocarbon	Product	Yield (%)
(dichloropyridine)	(dichloro-fluoropyridine)	84
(dichloropyrazine)	(dichloro-fluoropyrazine)	91
(chlorobenzene)	(trichloro-fluorobenzene)	60

now provide a simple laboratory synthesis of **3**. That is, the 2*H*-heptafluorobut-2-ene **2**, present in the product mixture, was converted quantitatively to **3** when a mixture of **3** and **2** was allowed to stand, in a sealed system, over 4 Å molecular sieves for 25 days. The alternative synthesis of **3** from **4** involves the use of antimony fluorides and/or hydrogen fluoride.[10]

A reasonable explanation for the unique formation of **3** in the system containing the PFC **1**, is that **3** is transferred rapidly to the perfluorocarbon layer and hence removed from access to the fluoride ion source, which otherwise promotes the conversion of **3** to **2**, Scheme 1.
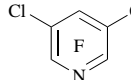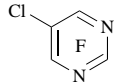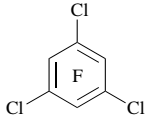
The reported reaction of octachlorocyclopentene with potassium fluoride provides a convenient laboratory synthesis of octafluorocyclopentene **8**,[8] and we now find that using only 25% of the normal THTD charge leads, in this case, to high conversions to **8** using either a Carius tube or atmospheric pressure conditions on a larger scale.

Similarly chlorofluoro-pyridines and -pyrimidines are commercial products and we find that the conditions described above can be applied equally to these systems and also to the synthesis of chlorofluorobenzene derivatives; these results are summarised in Table 1.

We hope that the results described above will be useful to workers who operate these systems on a larger scale and we envisage that the application of PFCs to systems with serious solvent recovery problems or systems with potentially serious heat-transfer problems will be particularly beneficial.

Our next objective was to reduce, still further, the hydrocarbon content of the reaction medium with the aim of essentially 'solventless' systems, where the fluorocarbon acts as a suspension medium. Consequently, we have examined a series of 'additives', to the fluorocarbon, with a view to coordinating the 'additive' to the potassium and therefore making the fluoride available. There is also the question of clearing the surface of the metal fluorides because electron spectroscopy for chemical analysis (ESCA) experiments with analytically pure

samples of potassium or caesium fluoride have previously revealed[11] only the corresponding chlorides on the surface! Thus *all* of the chloride impurity migrates to the surface of caesium or potassium fluoride.

The additives examined were water, tetraglyme, tetrabutylammonium bromide and 18-crown-6 **9**. Only the latter led to efficient fluorination, although tetrabutylammonium bromide has a significant effect. No fluorination was observed using either water or tetraglyme. In contrast, addition of **9** was effective down to levels as low as a 1% molar ratio, in relation to the chlorinated reactant, thus demonstrating the concept of potentially 'solventless' systems. However, the reactions proceeded relatively slowly at these concentrations and therefore, to effect shorter reaction times, we have employed systems containing 10 mol% of **9**.

The PFC is recovered essentially quantitatively by simple filtration from the residue. The polyether **9** is mixed with the residual metal salts in the filtrate at this stage but can be removed easily by extraction with acetone. Using these recovered materials without further purification but, of course, addition of fresh potassium fluoride, a second cycle of reaction was carried out with octachlorocyclopentene. However this was of reduced efficiency and some further purification of the recovered **9** would be required to maintain high efficiency in re-use. Examples of the application of this system to the synthesis of fluorinated aromatic compounds are shown in Table 2.

Returning to the reactions with hexachlorobutadiene **4** (see above), we find that the products from this reactant and the system containing 18-crown-6 **9**, remarkably, depend on the ratio of **9** used. When a molar ratio of 50% of **9** with **4** was used, the sole product was 2*H*-heptafluorobut-2-ene **2**; a ratio of 10% **9** gave hexafluorobut-2-yne **3** as the major product (72:10:18; **3**:**2**:**7**), while a 1% ratio and using a sealed system gave hexafluorocyclobutene **7** as the product (68%), with small quantities of **3** and **2**. These surprising findings now cast some light on the mechanism of these processes which have hitherto been difficult to establish. We have concluded that the only mechanism that accounts for the observations is that outlined in Scheme 1 and we assume that the availability of fluoride ion in the system is related directly to the concentration of polyether **9** used. Initial vinylic displacement of chloride by fluoride occurs giving hexafluorobutadiene **6** which, at low concentrations of fluoride ion, will be extracted preferentially into the fluorocarbon phase and then undergo the well established electrocyclisation[12] to **7**. This will also be favoured by the increased pressure associated with the use of a Carius tube. However, in the presence of higher ratios of fluoride, **6** is quickly converted to hexafluorobut-2-yne **3**, again by established processes.[13] This will then be extracted into the perfluorocarbon layer and consequently protected from further

reaction. However, at high concentrations of fluoride further reaction *i.e.* **3** to **5** to **2**, competes.

The conclusion that the process begins by vinylic displacement of chlorine by fluorine to give **6**, rather than by attack accompanied by allylic displacement, is confirmed further by the fact that conversion of **10** to octafluorobut-2-ene **11** (Scheme 2), is performed with very high efficiency and it is useful to note that this perfluoroalkene was hitherto relatively inaccessible.[14]
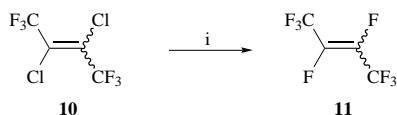
Scheme 2 *Reagents and conditions*: i, KF, 0.1 equiv. 18-crown-6 **9**, PFC **1**, 190 °C, 48 h (90%)

There remains the question of whether the potassium fluoride is actually taken into solution in the perfluorocarbon layer by the 18-crown-6 **9**, or whether the latter remains solely in suspension. We have heated potassium permanganate and potassium picrate separately with 18-crown-6 **9** and the perfluorocarbon **1**, and in neither case did we have clear evidence of colour generated in the perfluorocarbon layer which would have indicated solubility and it seems unlikely that fluoride salts would be more soluble. On this basis, therefore, we favour the conclusion that the 18-crown-6–potassium fluoride complex is essentially in suspension in the perfluorinated medium, as was described above of THTD but that the proportions of **9** required for activating the metal fluoride are *substantially* less than for THTD.

So far, the potassium fluoride–18-crown-6 system has not been successfully applied to selective fluorination of aliphatic or alicyclic systems. We have attempted displacement of the tosyl group by fluoride ion from 4-methylcyclohexyl toluene-*p*-sulfonate; reaction with Pr^{n}OSO$_2$CF$_3$ was similarly unsuccessful and no reaction occurred with carbon tetrachloride. However, these investigations were by no means exhaustive.

Experimental

All starting materials were obtained commercially and used as received. Sulfolane (tetrahydrothiophene 1,1-dioxide, THTD) was dried, prior to use, by distillation onto 4 Å molecular sieves and perfluoroperhydrophenanthrene PFC **1** (Flutec PP11, bp 215 °C, as supplied by F2 Chemicals Ltd.) was dried over 4 Å molecular sieves. ^{19}F and ^{1}H NMR spectra were recorded using either a Bruker AC 250, a Varian VXR 400S, or a Bruker AMX 500 NMR spectrometer. ^{13}C NMR spectra were recorded using either a Varian VXR 400S or a Bruker AMX 500 spectrometer (unless stated all samples run in CDCl$_3$, ^{19}F referenced to CFCl$_3$ and all *J* values given in Hz; p refers to a pentet). Infrared spectra were recorded on a Perkin-Elmer 1600 FT–IR spectrometer using KBr discs (solid samples), thin films between two KBr plates (liquid samples), or a sealed gas cell fitted with KBr plates (gas samples). GLC mass spectra were obtained using a VG Trio 1000 spectrometer linked to a Hewlett-Packard 5890 Series II gas chromatograph fitted with a 25 m cross linked silicone capillary column. Carbon, hydrogen and nitrogen elemental analyses were obtained using a Carlo Erba 440 Elemental Analyser.

Reactions using THTD

General procedure for reactions in Carius tubes. A Carius tube (60 cm^3), charged with potassium fluoride, PFC **1**, THTD and chlorocarbon, was evacuated, sealed and heated in a rotating oil bath maintained at 190 °C. After the reaction was completed the tube was opened and any volatile material transferred to a cold trap under reduced pressure. Further distillation under reduced pressure was carried out to afford a single product.

2H-*Heptafluorobut-2-ene* **2**.†—Hexachlorobuta-1,3-diene **4** (2.1 g, 8.1 mmol), potassium fluoride (4.7 g, 81 mmol), PFC **1**

(6.5 cm^3) and THTD (2 cm^3), heated for 15 h gave 2H-heptafluorobut-2-ene (1.1 g, 60%), bp 8–10 °C (lit.,[8] 7–8 °C); ν_{max}/cm^{-1} 1050–1400 (CF), 1733 (C=C) and 3100 (CH); δ_F(235 MHz) −62.5 (3F, d, $^3J_{H-F}$ 28.4, 1-F), −77.0 (3F, s, 4-F), −119.7 (1F, s, 3-F); δ_C(100 MHz) 102.7 (qm, $^2J_{C-F}$ 38.9, 2-C), 117.5 (qd, $^1J_{C-F}$ 272.4, $^2J_{C-F}$ 38.9, 4-C), 120.8 (q, $^1J_{C-F}$ 269.5, 1-CF$_3$), 152.2 (dqq, $^1J_{C-F}$ 282.4, $^2J_{C-F}$ 39.7, $^3J_{C-F}$ 5.4, 3-C); δ_H(250 MHz) 5.57 (dq, $^3J_{H-F}$ 28.4, $^3J_{H-F}$ 6.9, 2-H); *m/z* (EI$^+$) 182 (M$^+$, 17.2%).

Octafluorocyclopentene **8**.—Octachlorocyclopentene (3.4 g, 10 mmol), potassium fluoride (5.8 g, 100 mmol), PFC **1** (6.5 cm^3) and THTD (2 cm^3), heated for 15 h gave octafluoro-cyclopentene **8** (1.9 g, 89%), bp 26–28 °C (lit.,[15] 25.4–26.5 °C); ν_{max}/cm^{-1} 1769 and 1396 (C=C) and 986–1219 (CF); δ_F(376 MHz) −117.3 (2F, m, 3 and 5-F), −129.4 (1F, m, 4-F), −148.7 (1F, m, 1 and 2-F); δ_C(100 MHz) 109.1 (tpt, $^1J_{C-F}$ 278.0, $^2J_{C-F}$ 23.9, $^3J_{C-F}$ 4.9, 4-C), 110.3 (tqm, $^1J_{C-F}$ 260.1, $^2J_{C-F}$ 23.7, 3 and 5-C), 138.6 (dm, $^1J_{C-F}$ 297.9, 1 and 2-C); *m/z* (EI$^+$) 212 (M$^+$, 13.4%).

1,3,5-*Trichloro*-2,4,6-*trifluorobenzene*.—Hexachlorobenzene (1.0 g, 3.5 mmol), potassium fluoride (1.8 g, 31.6 mmol), PFC **1** (10 cm^3) and THTD (4.5 cm^3), heated for 200 h gave 1,3,5-trichloro-2,4,6-trifluorobenzene (0.7 g, 83%), mp 59–61 °C (lit.,[8] 57–61 °C) (Found: C, 30.3. C$_6$Cl$_3$F$_3$ requires C, 30.6%); ν_{max}/cm^{-1} 1603 (C=C) and 1445 (CF); δ_F(376 MHz, [^{2}H$_6$]-acetone) −114.8 (m); δ_C(100 MHz, [^{2}H$_6$]acetone) 108.7 (td, $^2J_{C-F}$ 22.3, $^4J_{C-F}$ 4.9, 1-C), 154.7 (dt, $^1J_{C-F}$ 249.8, $^3J_{C-F}$ 4.5, 2-C); *m/z* (EI$^+$) 234 (M$^+$, 100%), 236 (M$^+$, 98.7), 238 (M$^+$, 28.5).

3,5-*Dichloro*-2,4,6-*trifluoropyridine*.—Pentachloropyridine (2.5 g, 10 mmol), potassium fluoride (4.0 g, 70 mmol), PFC **1** (6.5 cm^3) and THTD (2 cm^3), heated for 15 h gave 3,5-dichloro-2,4,6-trifluoropyridine (1.1 g, 60%), bp 157–159 °C (lit.,[16] 159–160 °C) (Found: C, 29.6; N, 6.9. C$_5$Cl$_2$F$_3$N requires C, 29.7; N, 6.9%); ν_{max}/cm^{-1} 1358–1434 (CF) and 1569–1604 (CN); δ_F(376 MHz) −70.0 (2F, d, $^4J_{F-F}$ 13.9, 2 and 6-F), −93.8 (1F, t, $^4J_{F-F}$ 14.3, 4-F); δ_C(100 MHz) 104.4 (m, 3 and 5-C), 155.8 (ddd, $^1J_{C-F}$ 246.0, $^4J_{C-F}$ 17.2, $^4J_{C-F}$ 10.8, 2 and 6-C), 164.8 (dt, $^1J_{C-F}$ 265.5, $^4J_{C-F}$ 5.3, 4-C); *m/z* (EI$^+$) 201 (M$^+$, 100%), 203 (M$^+$, 55.2), 205 (M$^+$, 7.8).

5-*Chloro*-2,4,6-*trifluoropyrimidine*.—Tetrachloropyrimidine (2.2 g, 10 mmol), potassium fluoride (3.5 g, 60 mmol), PFC **1** (6.5 cm^3) and THTD (2 cm^3), heated for 15 h gave 5-chloro-2,4,6-trifluoropyrimidine (1.1 g, 60%), bp 115–116 °C (lit.,[17] 115 °C) (Found: C, 28.5; N, 16.5. C$_4$ClF$_3$N$_2$ requires C, 28.5; N, 16.6%); ν_{max}/cm^{-1} 1417 (CF) and 1598–1640 (CN); δ_F(235 MHz) −43.1 (1F, s, 2-F), −55.8 (2F, s, 4 and 6-F); δ_C(100 MHz) 99.5 (td, $^2J_{C-F}$ 30.9, $^4J_{C-F}$ 10.0, 5-C), 158.0 (dt, $^1J_{C-F}$ 230.0, $^3J_{C-F}$ 21.6, 2-C), 168.6 (ddd, $^1J_{C-F}$ 261.0, $^3J_{C-F}$ 16.4, $^3J_{C-F}$ 10.3, 4 and 6-C); *m/z* (EI$^+$) 168 (M$^+$, 100%), 170 (M$^+$, 58.3).

General procedure for reactions at atmospheric pressure. A round-bottomed flask (500 cm^3) fitted with a reflux condenser, charged with potassium fluoride, PFC **1** (70 cm^3), THTD (30 cm^3) and chlorocarbon was heated to 190 °C and the contents stirred mechanically. After the reaction was complete, the flask was allowed to cool and any volatile material transferred to a cold trap under reduced pressure. Further distillation under reduced pressure afforded a single product.

Octafluorocyclopentene **8**.—Octachlorocyclopentene (17.2 g, 50 mmol) and potassium fluoride (34.8 g, 600 mmol) heated for 2 d gave octafluorocyclopentene **8** (6.1 g, 58%); see above for spectroscopic data.

3,5-*Dichloro*-2,4,6-*trifluoropyridine*.—Pentachloropyridine (6.3 g, 25 mmol) and potassium fluoride (11.6 g, 200 mmol) were heated for 3 d. After this time the flask was allowed to cool and the contents filtered, leaving a bi-phasic mixture; the lower layer (PFC **1**) was colourless and the upper (THTD) was orange. The layers were separated and worked up independently. The PFC layer was extracted with toluene (3 × 70 cm^3) and the solvent removed by rotary evaporation yielding a

colourless oil which solidified. The THTD layer was distilled under reduced pressure and yielded an identical sample of this colourless material. The two samples were combined and gave 3,5-dichloro-2,4,6-trifluoropyridine (4.7 g, 93%); see above for spectroscopic data.

Hexafluorobut-2-*yne* **3**.—Hexachlorobuta-1,3-diene **4** (261 g, 1 mol) was added dropwise over 2 h to a mechanically stirred suspension of freshly dried potassium fluoride (500 g, 8.5 mol) in anhydrous THTD (0.3 dm^3) and PFC **1** (1 dm^3), maintained at 190 °C. The reaction was stirred for a further 4 h after the final addition of the diene, whilst volatile products (96 g) were collected in two sequential traps maintained at liquid air temperatures and were identified by comparison to authentic spectra as hexafluorobut-2-yne **3** (43% by ^{19}F NMR integration) and 2*H*-heptafluorobut-2-ene **2** (14.3%). The volatiles were condensed over 4 Å molecular sieves[6] under reduced pressure and allowed to stand at room temperature for 25 d. After this time further analysis of a representative sample showed that the volatiles contained only hexafluorobut-2-yne[10] **3** (91 g, 56% based on starting diene **4**); ν_{max}/cm^{-1} 1188 and 1279 (CF) and 2360 (C≡C); δ_F(235 MHz) −55.6 (s); δ_C(100 MHz) 30.0 (q, $^2J_{C-F}$ 19.4, 2 and 3-C), 113.9 (q, $^1J_{C-F}$ 259.8, 1 and 4-C).

Reactions using 18-crown-6

General procedure for reactions in Carius tubes. A Carius tube (60 cm^3), charged with potassium fluoride, PFC **1** (20 cm^3), 18-crown-6 **9** and chlorocarbon, was evacuated, sealed and heated in a rotating oil bath maintained at 190 °C. After the reaction was complete, the tube was opened and any volatile material transferred to a cold trap under reduced pressure. Additional distillation under reduced pressure was carried out to effect further purification.

Hexafluorocyclobutene **7**.—Hexachlorobuta-1,3-diene **4** (2.6 g, 10 mmol), potassium fluoride (5.8 g, 100 mmol) and 18-crown-6 **9** (0.3 g, 1 mmol), heated for 15 h gave hexafluorocyclobutene **7** (1.1 g, 68%), bp 0–2 °C (lit.,[18] 1.1 °C); ν_{max}/cm^{-1} 1794 and 1416 (C=C) and 980–1385 (CF); δ_F(471 MHz) −122.2 (2F, m, 3 and 4-F), −131.4 (1F, m, 1 and 2-F); δ_C(126 MHz) 114.1 (tm, $^1J_{C-F}$ 285.0, 3 and 4-C), 135.1 (dm, $^1J_{C-F}$ 337.5, 1 and 2-C); *m/z* (EI$^+$) 162 (M$^+$, 3.4%).

2H-*Heptafluorobut*-2-*ene* **2**.—Hexachlorobuta-1,3-diene **4** (2.6 g, 10 mmol), potassium fluoride (4.6 g, 80 mmol) and 18-crown-6 **9** (1.3 g, 5 mmol), heated for 15 h gave 2*H*-heptafluorobut-2-ene **2** (1.0 g, 55%); see above for spectroscopic data.

Octafluorobut-2-*ene* **11**.—2,3-Dichlorohexafluorobut-2-ene **10** (2.3 g, 10 mmol), potassium fluoride (2.3 g, 40 mmol) and 18-crown-6 **9** (0.3 g, 1 mmol), heated for 48 h gave (*E,Z*)-octafluorobut-2-ene (3:1 ratio) **11** (1.8 g, 90.0%), bp 0–5 °C (lit.,[14] 0.9 °C); ν_{max}/cm^{-1} (mixture of isomers) 1598 and 1727 (C=C) and 1115–1350 (CF); δ_F(471 MHz) *E*-isomer −71.9 (3F, m, 1-F), −162.7 (1F, m, 2-F); *Z*-isomer −69.3 (3F, m, 1-F), −145.9 (1F, m, 2-F); δ_C(126 MHz) *E*-isomer 117.7 (qdm, $^1J_{C-F}$ 273.1, $^2J_{C-F}$ 30.1, 1-C), 142.1 (m, 2-C); *Z*-isomer 117.2 (qdm, $^1J_{C-F}$ 272.2, $^2J_{C-F}$ 38.9, 1-C), 140–144 (br m, 2-C); *m/z* (EI$^+$) 200 (M$^+$, 10.1%).

1,3,5-*Trichloro*-2,4,6-*trifluorobenzene*.—Hexachlorobenzene (2.9 g, 10 mmol), potassium fluoride (4.6 g, 80 mmol) and 18-crown-6 **9** (0.3 g, 1 mmol), heated for 216 h gave 1,3,5-trichloro-2,4,6-trifluorobenzene (60% by GC–MS integration) and, presumably, 1,2,3,5-tetrachloro-4,6-difluorobenzene (40%); *m/z* (EI$^+$) 252 (M$^+$, 100%).

3,5-*Dichloro*-2,4,6-*trifluoropyridine*.—Pentachloropyridine (2.5 g, 10 mmol), potassium fluoride (4.0 g, 70 mmol) and 18-crown-6 **9** (0.3 g, 1 mmol), heated for 15 h gave 3,5-dichloro-2,4,6-trifluoropyridine (1.7 g, 84%); see above for spectroscopic data.

5-*Chloro*-2,4,6-*trifluoropyrimidine*.—Tetrachloropyrimidine (3.3 g, 15 mmol), potassium fluoride (4.6 g, 80 mmol) and 18-crown-6 **9** (0.4 g, 1.5 mmol), heated for 15 h gave 5-chloro-2,4,6-

trifluoropyrimidine (2.3 g, 91%); see above for spectroscopic data.

Octafluorocyclopentene **8**.—Octachlorocyclopentene (1.7 g, 5 mmol), potassium fluoride (3.5 g, 60 mmol) and 18-crown-6 **9** (0.1 g, 0.5 mmol), heated for 15 h gave octafluorocyclopentene **8** (1.1 g, 100%). The PFC slurry was then filtered and 18-crown-6 extracted from the inorganic residues using acetone (3 × 10 cm^3). The acetone was removed on a rotary evaporator and the 18-crown-6 used in a repeat reaction without further purification along with the recovered PFC, as follows. Octachlorocyclopentene (1.5 g, 4.4 mmol), potassium fluoride (3.5 g, 60 mmol) and the recovered material, heated for 15 h gave octafluorocyclopentene **8** (0.7 g, 75%); see above for spectroscopic data.

General procedure for reactions in stirred autoclaves. A stirred autoclave (500 ml), charged with potassium fluoride, PFC **1** (50 ml), 18-crown-6 **9** and chlorocarbon, was evacuated, sealed and heated in a furnace maintained at 190 °C, whilst being stirred continuously. After the reaction was complete the autoclave was cooled, opened and any volatile material transferred to a cold trap under reduced pressure. Additional distillation under reduced pressure was carried out to effect further purification.

Octafluorocyclopentene **8**.—Octachlorocyclopentene (5.0 g, 14.4 mmol), potassium fluoride (10.0 g, 172.4 mmol) and 18-crown-6 **9** (0.4 g, 1.4 mmol), heated for 120 h gave octafluorocyclopentene **8** (2.3 g, 74%); see above for spectroscopic data.

3,5-*Dichloro*-2,4,6-*trifluoropyridine*.—Pentachloropyridine (5.0 g, 20.0 mmol), potassium fluoride (10.0 g, 172.4 mmol) and 18-crown-6 **9** (0.5 g, 2.0 mmol), heated for 40 h gave 3,5-dichloro-2,4,6-trifluoropyridine (2.8 g, 69%) after filtration and extraction of the PFC layer with toluene (3 × 70 cm^3), removal of solvent and subsequent distillation; see above for spectroscopic data.

General procedure for reaction at atmospheric pressure. A round-bottomed flask (250 cm^3) fitted with a reflux condenser, charged with potassium fluoride, PFC **1**, 18-crown-6 **9** and chlorocarbon was heated to 190 °C and the contents stirred mechanically for 4 d. After this time the flask was allowed to cool and any volatile material transferred to a cold trap under reduced pressure. Additional distillation under reduced pressure was carried out to effect further purification.

3,5-*Dichloro*-2,4,6-*trifluoropyridine*.—Pentachloropyridine (5.0 g, 20 mmol), potassium fluoride (9.2 g, 159.2 mmol), PFC **1** (50 cm^3) and 18-crown-6 **9** (0.5 g, 2 mmol) gave 3,5-dichloro-2,4,6-trifluoropyridine (2.6 g, 65%) after filtration and extraction of the PFC layer with toluene (3 × 70 cm^3), removal of solvent and subsequent distillation; see above for spectroscopic data.

5-*Chloro*-2,4,6-*trifluoropyrimidine*.—Tetrachloropyrimidine (3.3 g, 15 mmol), potassium fluoride (5.0 g, 86.2 mmol), PFC **1** (20 cm^3) and 18-crown-6 **9** (0.7 g, 2.8 mmol) gave 5-chloro-2,4,6-trifluoropyrimidine (1.6 g, 69%); see above for spectroscopic data.

Hexafluorobut-2-*yne* **3**.—Hexachlorobuta-1,3-diene **4** (240.0 g, 0.9 mol) was added dropwise over 2 h to a mechanically stirred suspension of freshly dried potassium fluoride (580.0 g, 10.0 mol), 18-crown-6 **9** (26.4 g, 0.1 mol) and PFC **1** (1.5 dm^3), maintained at 190 °C. The reaction was stirred for a further 4 h after the final addition of the diene. Volatile products (83 g) were collected in two sequential traps maintained at liquid air temperatures and products were identified by comparison to authentic spectra as hexafluorobut-2-yne[19] **3** (72% by ^{19}F NMR integration), 2*H*-heptafluorobut-2-ene[8] **2** (10%) and hexafluorocyclobutene[18] **7** (18%); see above for spectroscopic data.

Acknowledgements

References

1 J. S. Moilliet, in *Organofluorine Chemistry Principles and Commercial Applications*, ed. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenum Press, New York, 1994, p. 195.
2 D. D. MacNicol and C. D. Robertson, *Nature*, 1988, **332**, 59.
3 D. S. L. Slinn and S. W. Green, in *Preparation, Properties and Industrial Applications of Organofluorine Compounds*, ed. R. E. Banks, Ellis Horwood, Chichester, 1982, p. 45.
4 A. T. Cates, *J. Hazard. Mater.*, 1992, 1.
5 R. D. Chambers, A. J. Roche and M. H. Rock, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1095.
6 R. D. Chambers and A. J. Roche, *J. Fluorine Chem.*, 1996, **79**, 121.
7 R. D. Chambers and A. J. Roche, *J. Fluorine Chem.*, 1996, **79**, 139.
8 J. T. Maynard, *J. Am. Chem. Soc.*, 1963, **28**, 112.
9 R. D. Chambers, A. J. Roche and J. F. S. Vaughan, *Can. J. Chem.*, 1996, **74**, 1925.
10 A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.*, 1949, **71**, 298.
11 R. D. Chambers and D. T. Clark, unpublished results.
12 E. W. Schlag and W. B. Peatman, *J. Am. Chem. Soc.*, 1964, **86**, 1676.
13 W. T. Miller, W. Frass and P. R. Resnick, *J. Am. Chem. Soc.*, 1961, **83**, 1767.
14 R. N. Haszeldine, *J. Chem. Soc.*, 1952, 4423.
15 A. L. Henne and K. A. Latif, *J. Am. Chem. Soc.*, 1954, **76**, 610.
16 R. D. Chambers, J. Hutchinson and W. K. R. Musgrave, *J. Chem. Soc.*, 1964, 3573.
17 E. Klauke, L. Oehlmann and B. Baasner, *J. Fluorine Chem.*, 1982, **21**, 495.
18 A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, 1947, **69**, 279.
19 Sample supplied by Aldrich Chemicals.