Reactions involving Fluoride Ion. Part 16.[1] Nucleophilic Attack on a Perfluorotetra-alkylethylene and a Synthesis of Perfluorotetramethylfuran †

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Reaction of perfluoro-3.4-dimethylhex-3-ene (1) with oxygen nucleophiles gives products arising from attack on (1) as well as products arising from attack on the isomer. perfluoro-3.4-dimethylhex-2-ene (4). A novel cyclisation and defluorination is described for the reaction of (1) with MeOH and Et₃N. giving perfluorotetramethylfuran. Reactions of (1) with difunctional nucleophiles give cyclic products and oxidation of (1) with KMnO₄ in acetone yields a diol. An unusual intramolecular nucleophilic displacement of fluoride from a perfluoroalkyl group is reported.

A NUMBER of systems have now been synthesised of the type $(R_F)_2C=C(R_F)_2$, where R_F = perfluoroalkyl [2-5] or is part of a perfluorocycloalkyl group,[6,7] but the chemistry of these systems is relatively undeveloped. This is in contrast, of course, to the considerable literature which exists on the chemistry of systems containing fluorine atoms that are directly attached to the double bond.[8]

Perfluoro-3,4-dimethylhex-3-ene is now available as a ca. 1 : 1 mixture of cis- and trans-isomers (1) by various routes [1-4] including the fluoride ion induced dimerisation of perfluorobut-2-ene [4] and, on an industrial scale,[2] the corresponding oligomerisation of tetrafluoroethylene. In this paper, we describe some reactions of the alkene (1) towards nucleophiles and its oxidation with permanganate.

One of the very interesting features of systems like (1) is the fact that although the double bond is, in many cases, very susceptible to nucleophilic attack there is no vinylic fluorine available for displacement. Consequently, reactions of (1) involve S_N2' processes and an unusual range of secondary reactions is made possible.[7]

Perfluoro-3,4-dimethylhex-3-ene (1) is unreactive to
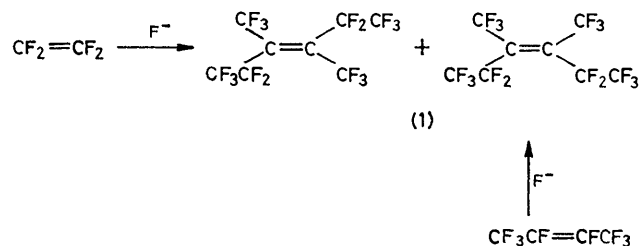
refluxing methanol but either a methyl ether (3; R = CH₃) or bis(methyl ether) (6; R = CH₃) may be obtained as the main product, depending on the conditions, from reaction with methanol in tetraglyme and using sodium carbonate as base. An additional minor product (5; R = CH₃) is also obtained and, indeed, this is the major product in a reaction under comparable conditions but using caesium fluoride as the base. Isomers (3; R =

CH₃) and (5; R = CH₃) are not, however, interconverted under the conditions of these reactions. It is interesting to note that, in the formation of (3; R = CH₃) the
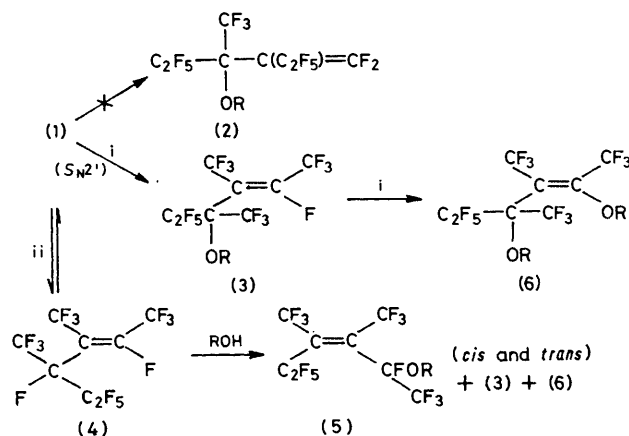
Reagents: i, ROH, tetraglyme, Na₂CO₃, 22°, 24 h; ii, ROH, tetraglyme, CsF, 22°, 20 h

fluorine is displaced from difluoromethylene groups and not trifluoromethyl, which would lead to the isomer (2; R = CH₃). This is consistent with the well known difficulty of removing fluorine from trifluoromethyl groups,[9] and also the fact that base catalysed reaction of methanol with perfluoro-2,3-dimethylbut-2-ene gave only addition,[5] rather than the substitution observed with (1). Clearly, (3; R = CH₃) is the product arising from S_N2' displacement from (1) while the methyl ether (5; R = CH₃) arises by vinylic displacement from (4), an isomer of (1) produced by equilibration with fluoride ion. The isomer (4) has not been characterised and the equilibrium constant between (1) and (4) in the presence of fluoride ion lies very largely on the side of (1). Nevertheless, the isomer (4) has a vinylic fluorine and such a structure would normally be more reactive than the isomer (1). This will account for the much higher yield of (5; R = CH₃) (53%) than (3; R = CH₃) (8%) in the presence of caesium fluoride. A similar range of products was also obtained using ethanol and propan-2-ol.

Using methanol with pyridine, triethylamine, or trimethylamine as the base with (1) gave, as well as methyl ethers, a fascinating cyclisation reaction. A deficiency of methanol in (1) in the presence of excess of pyridine led to the cyclic product (7). Also, in a separate experiment, it was shown that (5) is converted into (7)

reaction with alcohol arising from an S_N2' displacement on (10).

The cyclisation induced by triethylamine is even more intriguing because, in this case, perfluorotetramethylfuran (12) is one of the products. Furthermore, when (7) is heated under reflux with triethylamine, then (12) is
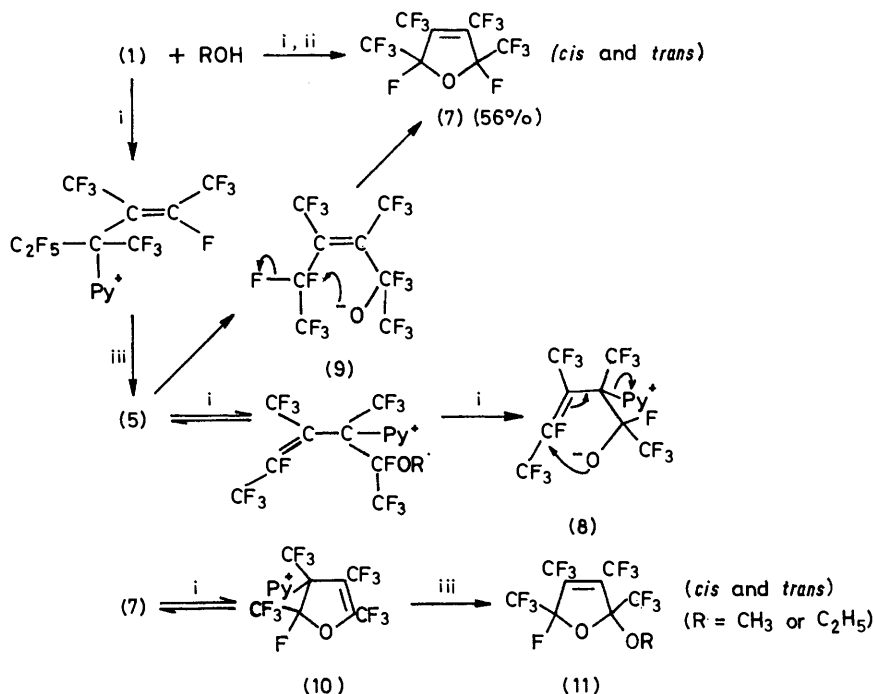
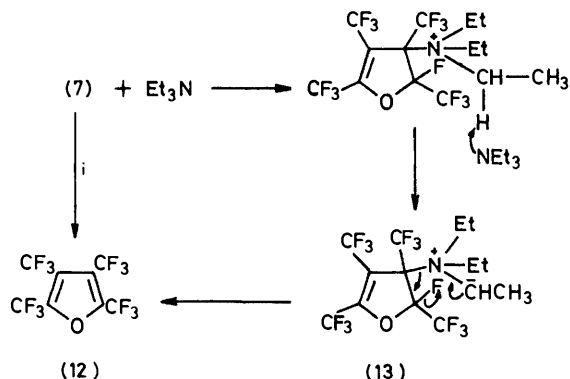

Reagents: i, pyridine; ii, tetraglyme, reflux; iii, ROH

either in the presence of pyridine or caesium fluoride. Obviously, the process involves generation of an oxygen anion by nucleophilic cleavage of the ether (5), accompanied by cyclisation. A cyclisation process involving an intramolecular S_N2' displacement of pyridine from (8) is the type of mechanism with most precedent in fluorinated systems. However, an example given later demonstrates, by analogy, that cyclisation via (9) is possible and, indeed, now seems most likely. The cyclic

Reagent: i, Fe, 580° (79% yield)

product (7) is obviously in equilibrium with (10), in the presence of pyridine, since (11) is the product of further

obtained in 41% yield. The most obvious possibility for this novel defluorination is that the process is induced by fluoride ion since defluorinations of this type have been noted previously.[1,10,11] We were unable, however, to effect *any* defluorination by heating (7) with caesium fluoride in tetraglyme. Also, as indicated above, no defluorination occurs with pyridine. Therefore, the process which we favour to account for these results involves formation and subsequent decomposition of the ylide (13). It is also possible to consider processes involving electron transfer from the amine but the contrasting results obtained with pyridine and triethylamine make these seem unlikely.

Perfluorotetramethylfuran (12) may, however, be obtained very efficiently by defluorination of (7) over iron at 580 °C.

Reaction of (1) with ethylene glycol in tetraglyme gave a cyclic product (14), corresponding to the dimethoxy compound (6). In contrast, intermolecular reaction is apparently more important with ethanolamine, since only an 8% yield of a cyclic product (15) is obtained, together with water soluble products.

Reactions of (1) with phenol produce a slightly different type of product mixture from those obtained using alcohols. In this case the monophenoxy derivatives are a mixture containing isomer (5; R = Ph) but, instead of (3), a different isomer (16; R = Ph) is present. In

separate experiments it has been demonstrated that compounds (5; R = Ph) and (16; R = Ph) are in

(1) + (CH$_2$OH)$_2$ $\xrightarrow{\text{i, ii}}$ (14) (58%)

(1) + HOCH$_2$CH$_2$NH$_2$ $\xrightarrow{\text{ii}}$ (15) (8%)
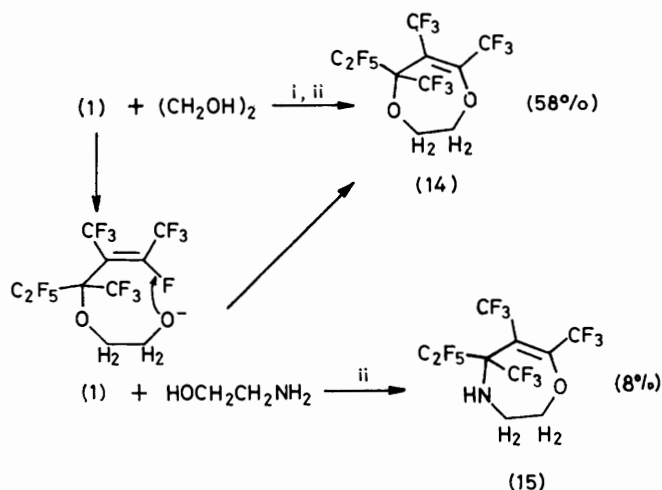
Reagents: i, Na$_2$CO$_3$; ii, tetraglyme

equilibrium in the presence of fluoride ion. Therefore, it seems likely that the formation of isomer (16) in the reaction with phenol but not in the analogous reactions with alcohols occurs because of the lower nucleophilic character of the oxygen atom in the enol ether (16; R = Ph) than in (16; R = alkyl). The alkyl derivatives are probably sufficiently nucleophilic to promote the conversion of (16) into (5).


(16) ⇌ (5)
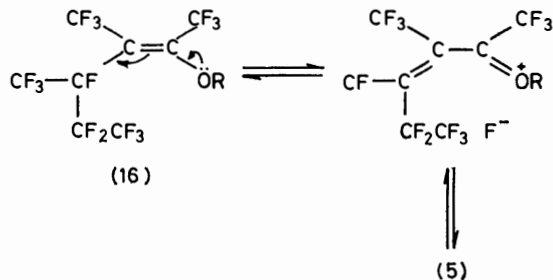
The absence of significant amounts of isomer (3; R = Ph) most likely stems from the lower reactivity of phenoxide than alkoxide ion. Consequently, as soon as sufficient fluoride ion is formed to set up the equilibrium between (1) and the more reactive isomer (4), then attack on the more reactive (4), by phenoxide ion, takes place leading to (5; R = Ph) and (16; R = Ph). In contrast alkoxide ions obviously react directly with (1) as well as with (4).

A cyclisation related to the formation of (7), discussed earlier, has been observed in reaction of the olefin (17) with aqueous base. The intermediate (18) is formed and the keto-form may be isolated after subsequent reaction with acid.[12] However, the important point to note is that conversion of (18) into (19) can only occur *via* an intramolecular nucleophilic displacement from a difluoro-methylene group. There is little precedent for this reaction in organofluorine chemistry;[8b] indeed it is well known that perfluoro-alkyl groups are inert to direct

nucleophilic attack, although S_N2' processes occur readily. Clearly, no S_N2' scheme can be written for the conversion of (18) into (19) and this reaction suggests that the formation of (7) occurs *via* an analogous cyclisation of (9).

Fluoro-olefins react readily with potassium permanganate in acetone [13] indicating, therefore, that this reagent has the characteristics of a nucleophile. Cor-

(17) $\xrightarrow[\text{Et}_3\text{N}]{\text{H}_2\text{O}}$ (18) → (19) (78%)
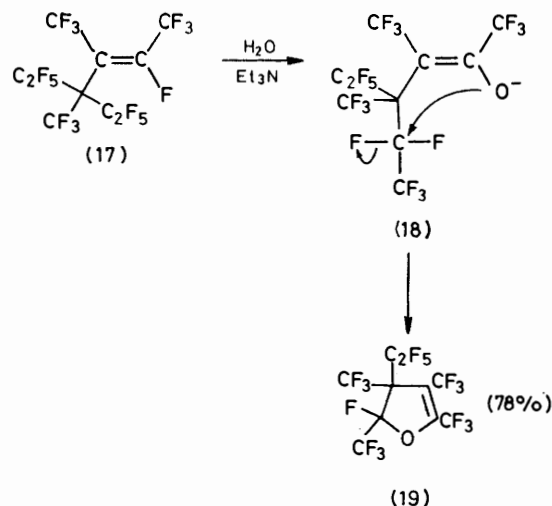
respondingly, we have obtained a diol (20) from a reaction of (1) with this reagent.

(1) $\xrightarrow[\text{acetone}]{\text{KMnO}_4}$ CF$_3$CF$_2$—C(CF$_3$)(OH)—C(CF$_3$)(OH)—CF$_2$CF$_3$ (65%)

(20)
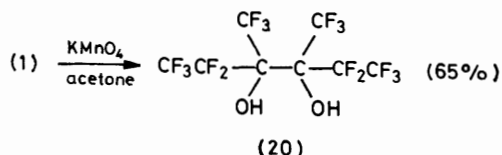
Structural Assignments.—Structures of the various products derived from (1) were easily deduced from ^{19}F chemical shifts and relative intensities by comparison with the [19]F n.m.r. data for compounds (1) and (17) [2] (see

[19]F N.m.r. data for model compounds

	δ (p.p.m.) (Assignment)	
(1a)	58.0 (3a,4a) 74.5 (1,6) 99.8 (2,5)	
(1b)	57.2 (3a,4a) 74.5 (1,6) 99.8 (2,5)	
(17)	51.9 (3a) 56.9 (4a) 67.4 (1) 75.9 (2) 79.2 6,6′ 105.8 5,5′	$J_{1,3a}$ 15.7 Hz $J_{1,2}$ 1.5 Hz

Table) which contain the relevant structural features. Assignments are contained in the Experimental section.

was stirred for a further 20 h and then the product (9.1 g) was isolated as described in (a). The product mixture was
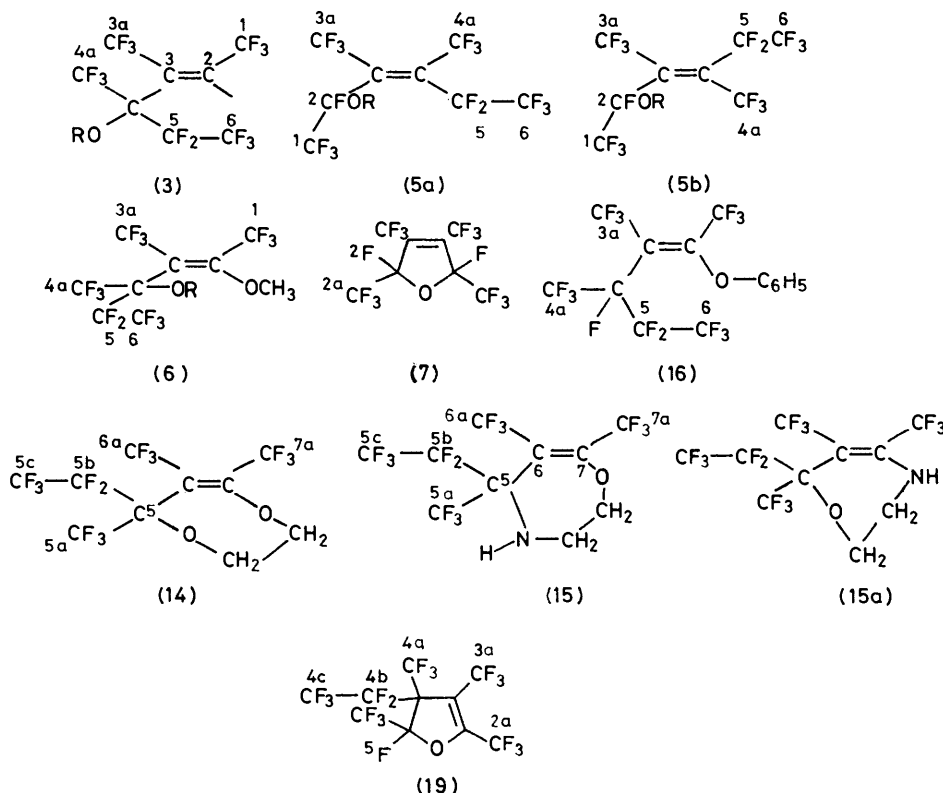
Numbering systems for n.m.r. assignments

EXPERIMENTAL

[19]F and [1]H n.m.r. spectra were measured at 40° using a Varian A56/60D spectrometer, with trichlorofluoromethane or tetramethylsilane as external reference. Upfield shifts are quoted as positive. Unless otherwise stated, percentage yields and conversions were determined by g.l.c. analysis (using a gas-density balance detector) of the crude product mixture.

Reactions of Perfluoro-3,4-dimethylhex-3-ene (1) *with Methanol using Different Bases.*—(a) *Using sodium carbonate.* A mixture containing (1) (10 g, 25 mmol), methanol (0.75 g, 23.4 mmol), anhydrous sodium carbonate (2.5 g, 23.6 mmol), and tetraglyme (20 ml) was stirred vigorously over 24 h. The mixture was then poured into water, where the products (8 g) separated as a lower layer. Analysis by g.l.c. showed one major product, with two minor components. Separation of a sample by preparative scale g.l.c. (78°; di-isodecyl phthalate) gave *trans*-4-*methoxy*-3,4-*bistrifluoromethylnonafluorohex*-2-*ene* (3; R = CH$_3$) (61%, 67% conversion, based on g.l.c. analysis) (Found: F, 68.7%; M^+ — F, 393. C$_9$H$_3$F$_{15}$O requires F, 69.2%; M^+, 412); b.p. 122°, $v_{max.}$ 1 660 cm.$^{-1}$ (C=C str.); δ_F (3 F, 3a-F), 67 (3 F, 4a -F), 70 (3 F, 1-F, $J_{1,2}$ 3, $J_{1,3a}$ 13 Hz), 82 (3 F, 6-F), 93 (1 F, 2-F), and 120 (2 F, 5-F); δ_H 3.7 (s). The g.l.c. retention times of minor products coincided with those of (5) and (6), see later.

(b) *Using caesium fluoride.* Methanol (1 g, 31.3 mmol) was added, dropwise over 4 h, to a stirred mixture containing (1) (10 g, 25 mmol), caesium fluoride (3 g, 19.7 mmol), and tetraglyme (20 ml) at room temperature. The mixture

separated by micro-distillation (Fischer–Spaltrohr) into a residue and two fractions boiling at *ca.* 130 and 134° and the volatile fractions were further separated by preparative-scale g.l.c. (60°; silicone elastomer) giving (3) (8% yield), identified by comparison of spectroscopic data [see (a)] and *cis*- and *trans*-2-methoxy-3,4-bistrifluoromethylnonafluoro-hex-3-ene (5; R = CH$_3$) (53%) (Found: C, 26.5; F, 68.6%; M^+, 412); b.p. 126.5°; $v_{max.}$ 1 645 cm^{-1} (C=C str.); δ_F 58 and 59 (6 F, 3a- and 4a-F), 72 and 75 (6 F, 1- and 6-F), 100 (2 F, 5-F), and 112 (1 F, 2-F) p.p.m.; δ_H 3.7, (s). The presence of two isomers in *ca.* 1 : 1 ratio was deduced from the fact that partial resolution could be achieved by g.l.c. and, in addition, the resonance at δ 75 p.p.m. in the [19]F n.m.r. spectrum, although of intensity equivalent to 3F, was partly resolved into two signals, one a doublet and one a multiplet. Preparative-scale g.l.c. on the distillation residue (140°; di-isodecyl phthalate) gave trans-2,4-*dimethoxy*-3,4-*bistrifluoromethyloctafluorohex*-2-*ene* (6; R = CH$_3$) (17%) (Found: F, 62.9; C, 28.1%; M^+ — F, 405. C$_{10}$H$_6$F$_{14}$O$_2$ requires F, 62.7; C, 28.3%; M^+, 424); b.p. 161°; $v_{max.}$ 1 620 cm^{-1} (C=C str.); δ_F 53 (3 F, 3a-F), 63 (3 F, 1-F, $J_{1,3a}$ 17 Hz), 64 (3F, 4a-F), 80 (3 F, 6-F), and 118 (2 F, 5-F) p.p.m.; δ_H 3.7 (4-OCH$_3$) and 4.0 (2-OCH$_3$).

(c) *Using triethylamine.* Methanol (0.75 g, 23.4 mmol) was added dropwise to a vigorously stirred mixture containing (1) (10 g, 25 mmol), triethylamine (5 g, 49.5 mmol), and tetraglyme (20 ml). The product mixture (9.5 g) was isolated as described in (a) and then separated by preparative-scale g.l.c. (78°; di-isodecyl phthalate) giving (3) (18%) and (5) (9%), identified by comparison of spectra

and *cis*- and *trans*-perfluoro-2,5-dihydrotetramethylfuran
(7) (22%) (Found: C, 25.3%, M^+ − F, 359. Calc. for
C_8F_4O: C, 25.4%, M^+, 378); b.p. 83°; $\nu_{max.}$ 1 700 cm^{-1}
(C=C str.); δ_F (Isomer A, 65%) 63 (3F, 3a-F), 85 (3F, 2a-
F), and 122 (1F, 2-F) p.p.m.; (Isomer B, 35%) 62 (3F, 3a-
F), 83 (3 F, 2a-F), and 112 (1F, 2-F) p.p.m. The other
minor components in the mixture were not identified.

(d) *Using triethylamine under reflux.* A reaction analo-
gous to that described under (c) was carried out except that
methanol (0.75 g, 23.4 mmol) was added to the mixture
under reflux and the reflux was maintained for 4 h before
work-up. The product mixture was isolated as described
under (a) and from this a volatile liquid (5.1 g) was removed
under vacuum from a black residue. Analysis of the vola-
tile liquid by g.l.c. showed the presence of (3) (17.5% yield)
and (7) (30%) and the remaining component of the mixture
was identified as *perfluorotetramethylfuran* (12) (8%) after
isolation by preparative-scale g.l.c. (Found: F, 67.6%; M^+,
340. $C_8F_{12}O$ requires F, 67.0%; M^+, 340); b.p. 103°;
$\nu_{max.}$ 1 640 cm^{-1} (C=C str.); δ_F 60 and 65 p.p.m. (2a- and
3a-F, unassigned).

(e) *Using pyridine.* A reaction analogous to (d) using
methanol (0.75 g, 23.4 mmol) was carried out except that
pyridine (4 g, 50.6 mmol) was used in place of triethylamine.
The product mixture (6.5 g) contained (1) together with
perfluoro-2,5-dihydrotetramethylfuran (7) (56%).

Reactions of Compound (7).—(a) *With triethylamine
under reflux.* A mixture containing (7) (2 g, 5.3 mmol),
triethylamine (1 g, 9.9 mmol), and tetraglyme (5 ml) was
heated in a sealed glass tube at 95° for 20 h. After cooling,
volatile material (1.2 g) was transferred under vacuum from
the tube and contained, by g.l.c. (silicone elastomer; 80°),
(7) (61%) and (12) [39%, 41%, based on (7) consumed].
Involatile material (0.5 g) was recovered from the tetra-
glyme layer on addition of water.

(b) *With pyridine.* In a reaction analogous to that
described under (a) but using pyridine, (7) was recovered.

Conversion of Compound (5; R = C_2H_5) *into* (7).—A
stirred mixture containing (5) (1 g, 2.3 mmol), pyridine
(0.21 g, 2.7 mmol), and tetraglyme (5 ml) was heated in a
sealed glass tube at 120° for 2 h. After cooling, volatile
material was transferred under vacuum from the tube,
washed with dilute HCl, and analysis of the product
(0.4 g) by ^{19}F n.m.r. spectroscopy and g.l.c. showed that the
sample contained >95% (7) (43% yield).

A similar mixture but containing caesium fluoride instead
of pyridine, was heated at 110° for 21 h and (7) (34%) was
transferred from the tube.

Reaction of Compound (7) *with Ethanol.*—A mixture
containing ethanol (0.26 g, 5.7 mmol), (7) (2.2 g, 5.8 mmol),
pyridine (0.46 g, 5.8 mmol), and tetraglyme (5 ml) was
stirred for 11 days. The lower layer (1.6 g) was separated,
transferred under vacuum from phosphorus pentaoxide,
and contained (11; R = C_2H_5) (90%; 61% yield) and
five minor components. A sample was separated by pre-
parative-scale g.l.c. (silicone elastomer; 100°) giving *cis*-
and *trans*-2-ethoxy-5-fluorotetratrifluoromethylfuran (11;
R = C_2H_5), b.p. 125—126° (Found: C, 30.0; F, 60.6%;
M^+ − H, 403. Calc. for $C_{10}H_5F_{13}O_2$: C, 29.7; F, 61.1%;
M^+, 404); $\nu_{max.}$ 1 700 cm^{-1} (C=C str.); δ_F (Isomer A, 83%)
61 (6F, 3a- and 4a-F), 80 and 81 (6F, 2a- and 5a-F), and
106 (1F, 5-F) p.p.m.; (Isomer B, 17%) 62 (6F, 3a- and 4a-
F), 82 (6F, 2a- and 5a-F), and 114 (1F, 5-F) p.p.m.; δ_H
1.4 (3 H) and 3.7 (2 H).

Reaction of Compound (1) *with Ethanol.*— Ethanol (2.6 g,

56.5 mmol) was added over 2 h to a stirred mixture of (1)
(20 g, 50 mmol), caesium fluoride (7.7 g, 50.7 mmol), and
tetraglyme (35 ml) at room temperature. After a further
period of 18 h, water (150 ml) was added, the lower layer
was separated and dried (Na_2SO_4), giving a liquid (19 g)
containing three main components, separated by distillation
followed by preparative-scale g.l.c. (60 and 180°; silicone
elastomer); yields were calculated by analytical scale v.p.c.
giving cis- and trans-2-*ethoxy*-3,4-*bistrifluoromethylnona-
fluorohex*-3-*ene* (5; R = CH_2CH_3) (40%), b.p. 132°(Found:
C, 28.2; F, 66.5%; M^+, 426. Calc. for $C_{10}H_5F_{15}O$: C, 28.2;
F, 66.9%; M^+, 426); $\nu_{max.}$ 1635 cm^{-1} (C=C str.); δ_F 58 and
59 (6F, 3a- and 4a-F), 72 and 75 (6F, 1-, 6-F), 101 (2F, 5-F),
112 (1H, 2-F) p.p.m.; δ_F 1.4 (3H) and 4.0 (2H) p.p.m.;
trans-4-*ethoxy*-3,4-*bistrifluoromethylnonafluorohex*-2-*ene*
(3; R = CH_2CH_3) (23%), b.p. 128.5° (Found: C, 28.2;
F, 66.6%; M^+ − H, 425); $\nu_{max.}$ 1 660 cm^{-1} (C=C str.);
δ_F 54 (3F, 3a-F), 66 (3F, 4a-F), 68 (3F, 1-F, $J_{1,3a}$ 15, $J_{1,2}$
2 Hz), 81 (3F, 6-F), 92 (1F, 2-F), 118 (2F, 5-F) p.p.m;
δ_H 1.3 (3 H) and 3.8 (2 H); and trans-2,4-*diethoxy*-3,4-
bistrifluoromethyloctafluorohex-2-*ene* (6; R = CH_2CH_3)
(7%), b.p. 180° (Found: C, 32.0; F, 58.3%; M^+, 452.
$C_{12}H_{10}F_{14}O_2$ requires C, 31.9; F, 58.8%; M^+, 452); $\nu_{max.}$
1 615 cm^{-1} (C=C str.); δ_F 53 (3F, 3a-F), 62 (3F, 1-F, $J_{1,3a}$ =
17 Hz), 63 (3F, 4a-F), 80 (3F, 6-F), 117 (2F, 5-F) p.p.m.;
δ_H 1.4 (3 H) and 4.0 (2 H).

Reaction of Compound (1) *with Phenol.*—A mixture con-
taining (1) (10 g, 25 mmol), triethylamine (5 g, 50 mmol),
phenol (2.4 g, 25.5 mmol), and tetraglyme (20 ml) was
stirred, vigorously, at room temperature for 16 h. The
mixture was poured into water (20 ml) and the product
(10.9 g) separated as a lower layer. Analysis by g.l.c.
(125°; di-isodecyl phthalate), followed by separation of
samples on a preparative scale gave trans-2-*phenoxy*-3,4-
bistrifluoromethylnonafluorohex-3-*ene* (5b; R = C_6H_5) (28%),
b.p. 194° (Found: C, 35.4; F, 60.4%; M^+, 474. $C_{14}H_5$-
$F_{15}O$ requires C, 35.5; F, 60.1%; M, 474); $\nu_{max.}$ 1 675 cm^{-1}
(C=C str.); δ_F 58 (6F, 3a- and 4a-F), 71 (3F, 1-F), 76 (3F,
6-F), 100 (2F, 5-F), and 106 (1F, 2-F) p.p.m.; δ_H 7.8;
cis-2-*phenoxy*-3,4-*bistrifluoromethylnonafluorohex*-3-*ene* (5a;
R = C_6H_5) (37%), b.p. 193° (Found: C, 35.6; F, 60.4%;
M^+, 474); $\nu_{max.}$ 1 635 cm^{-1} (C=C str.); δ_F 59 (6F, 3a- and
4a-F), 71 (3F, 1-F), 75 (3F, 6-F, $J_{2,6}$ 21 Hz), 99 (2F, 5-F),
and 106 (1F, 2-F) p.p.m.; δ_H 7.8; and trans-2-*phenoxy*-3,4-
bistrifluoromethylnonafluorohex-2-*ene* (16; R = C_6H_5) (35%),
b.p. 191° (Found: C, 35.7; F, 60.4%; M^+, 474); $\nu_{max.}$
1 650 cm^{-1} (C=C str.); δ_F 59 (3F, 3a-F), 60 (3F, 1-F, $J_{1,3a}$
15 Hz), 73 (3F, 4a-F), 83 (3F, 6-F, $J_{4,6}$ 18 Hz), 118 (2F,
5-F), and 181 (1F, 4-F) p.p.m.; δ_H 7.8.

Equilibration of Phenyl Ethers.—A mixture of phenyl
ethers (5a; R = C_6H_5), (5b; R = C_6H_5), and (16, R =
C_6H_5) of known composition, determined by g.l.c. (125°;
di-isodecyl phthalate) was stirred with molar quantities
of caesium fluoride in tetraglyme as solvent for 36 h at
room temperature. The phenyl ethers were recovered by
adding water and the final composition was determined as
for the starting material. The results of this and a similar
experiment in which triethylamine was used instead of
caesium fluoride are given below.

	(5a)	(5b)	(16)
Initial composition (%)	29	13	58
After stirring with CsF	37.5	25	37.5
After stirring with Et_3N	32	19	49

Reaction of Compound (1) *with Ethylene Glycol.*—A
mixture containing (1) (10.1 g, 25.3 mmol), ethylene glycol

(1.75 g, 28.2 mmol), sodium carbonate (5 g, 47.2 mmol), and tetraglyme (20 ml) was stirred over a period of 42 h. The product (6.9 g) separated as a lower layer on addition of water (50 ml). Analysis by g.l.c. (160°; silicone elastomer) showed one major product, and separation of a sample by preparative-scale g.l.c. gave 5-*pentafluoroethyl*-5,6,7-*tristrifluoromethyl*-1,4-*dioxacyclohept*-6-*ene* (14) (58%), b.p. 183.5° (Found C, 28.7; F, 62.5%; M^+, 422. $C_{10}H_4F_{14}O_2$ requires C, 28.5; F, 63.0%; M, 422); $v_{max.}$ 1 620 cm^{-1} (C=C); δ_F 53 (3 F, 6a-F), 67 (3 F, 5a-F), 70 (3F, 7a-F, $J_{7a,6e}$ 15.5 Hz), 80 (3F, 5c-F), and 118 (2 F, 5b-F) p.p.m.; δ_H 4.5.

Reaction of Compound (1) *with Ethanolamine.*—Ethanolamine (4.5 g, 73.6 mmol) was added slowly to a stirred mixture of (1) (10 g, 25 mmol) and tetraglyme (20 ml). After 1 h, water (50 ml) was added and the product (3g) separated as a lower layer. Analysis by g.l.c. (170°; silicone elastomer) showed four components. Preparative-scale g.l.c. gave 5-*pentafluoroethyl*-5,6,7-*tristrifluoromethyl* 1-*oxa*-4-*azacyclohept*-6-*ene* (15) (8%) (Found: M^+, 421. $C_{10}H_5F_{14}NO$ requires M^+, 421); $v_{max.}$ 1 610 (C=C) and 3 395 cm^{-1} (N–H); δ_F 53 (3F, 6a-F), 65 (3F, 5a-F), 70 (3F, 7a-F, $J_{7a,6a}$ 16 Hz), 79 (3F, 5c-F), and 117 (2F, 5b-F, AB, J 290 Hz) p.p.m.; δ_H 3.0 (1 H, 4-H), 3.8 (2 H, 3-H), and 5.0 (2 H, 2-H). The spectral data do not distinguish between the structure assigned to (15) and an isomer (15a), but the isomer (15a) would almost certainly exist as its tautomer.

Reaction of Compound (1) *with Potassium Permanganate.*—To a solution of potassium permanganate (4.7 g, 29.7 mmol) in dry acetone (100 ml), (1) (9.7 g, 24.3 mmol) was added slowly. After stirring for 3 h water (100 ml) was added and sulphur dioxide was bubbled into the mixture to decolourise. On cooling to 0° a lower layer formed, which was separated, and after addition of water (100 ml) was extracted into carbon tetrachloride. After washing and drying (MgSO$_4$ then P$_2$O$_5$) carbon tetrachloride was removed by distillation and the last traces by bubbling nitrogen through the product at 100° to give 3,4-*bistrifluoromethyl-decafluorohexane*-3,4-*diol* (20) (65%), m.p. 49—51° (Found: C, 22.0; F, 69.5%; M^+, 434. $C_8H_2F_{16}O_2$ requires C, 22.1; F, 70.0%; M^+, 434); δ_F (ether) 70 (3F 3a- and 4a-F), 80 (3F, 1- and 6-F), and 111 (2F, 2- and 5-F) p.p.m.; δ_H 6.1.

Defluorination of Compound (7) *over Iron.*—Perfluoro-2,5-dihydrotetramethylfuran (7) (9.95 g) was passed through a hot silica glass tube packed with iron filings (580°) in a stream of nitrogen. The product (7.55 g), which was collected in a liquid air cooled trap, contained, by ^{19}F n.m.r., (7) (23% by weight) and (12) [77%, 79% yield based on (7) consumed]. The product was distilled (Fischer–Spaltrohr) to give, as the residue, (12) (3.65 g, 49% isolated yield).

Preparation of Perfluoro-4-ethyl-2,3,4,5-tetramethyl-4,5-dihydrofuran (19).—A mixture containing (17) (1 kg, 2 mol), diglyme (100 g), distilled water (40 g, 2.2 mol), and Monoflor 31 (a fluorinated surfactant to aid emulsification) (ca. 10 drops) was stirred vigorously in a three-necked flask (3 l) fitted with air-powered stirrer, thermometer, dropping funnel, and water condenser. Triethylamine (420 g, 4.2 mol) was added, dropwise, over 3.5 h while maintaining the temperature at <28° with the aid of a large water-bath for cooling and then the mixture was stirred at ambient temperature overnight. Distillation of the mixture gave a fraction, b.p. 80—120 °C, which separated on collection into triethylamine and a lower fluorochemical layer. This lower layer was removed, washed with acetone (3 × 50 ml), dilute HCl (3 × 250 ml), water (2 × 250 ml), and was then dried (Na$_2$SO$_4$). The resultant product (746 g, 78%) was >98% pure, as determined by analytical scale g.l.c. giving *perfluoro-4-ethyl-2,3,5,6-tetramethyl-4,5-dihydrofuran* (19) (Found: C, 25.1; F, 71.1; M^+, 478. $C_{10}F_{18}O$ requires C, 25.1; F, 71.5%; M^+, 478); $v_{max.}$ 1 695 cm^{-1} (C=C str.); δ_F 57 (3F, 3a-F), 66 (3F, 4a-F), 69 (3F, 2a-F, $J_{2a,3a}$ 9 Hz), 77 (3F, 5a-F, $J_{5,5a}$ 36 Hz), 79 (3F 4c-F), 103 (2F, 4b-F), 117 (1F, 5-F) p.p.m.

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