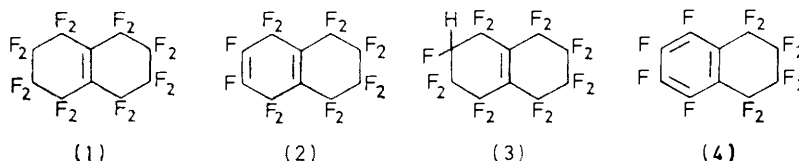# Fluorinations with Complex Metal Fluorides. Part 4.[1] An Improved Synthesis and the Oxidation of Hexadecafluorobicyclo[4.4.0]dec-1(6)-ene

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Fluorination of naphthalene,tetralin, and decalin with caesium tetrafluorocobaltate(III) yielded two major products identified as hexadecafluorobicyclo[4.4.0]dec-1(6)-ene and dodecafluorotetralin. Oxidation of the alkene gave cis-hexadecafluorobicyclo[4.4.0]decane-1,6-diol. Some reactions of this diol (e.g. with diazomethane, benzoyl chloride, and thionyl chloride) are described.

NAPHTHALENE[2] and tetralin[3] have been fluorinated exhaustively over cobalt(III) fluoride, resulting in good conversions into perfluorodecalin, which was separated subsequently into cis- and trans-isomers.[4] Under milder conditions, a complex mixture of polyfluorides was obtained,[5] apparently largely polyfluorodecalins having one or two hydrogen substituents. With potassium tetrafluorocobaltate(III),[6] although this is in general a milder reagent than cobalt(III) fluoride, the main products of fluorination were compounds (1)—(3) which all retained a double bond between the ring-junction carbon atoms.[7]

When caesium tetrafluorocobaltate(III) is used as a fluorinating agent,[8] aromatic polyfluorides are found among the products; that from benzene was shown to contain a series of polyfluorobenzenes including hexafluorobenzene. This observation prompted the present study of the fluorinations of naphthalene, tetralin, and decalin over the caesium salt. After treatment in the usual way[9] at 350—380 °C, the product mixtures were separated by g.l.c.; their compositions are recorded in the Table.

The absence of octafluoronaphthalene was confirmed by g.l.c. enrichment techniques. The unresolved components were not polyfluorodecalins; i.r. spectroscopy showed absorptions characteristic of polyfluoroaromatic compounds. The major product, hexadecafluorobicyclo[4.4.0]dec-1(6)-ene (1) was identical with that obtained from the fluorination of octafluoronaphthalene with cobalt(III) fluoride.[10] The other main product, dodecafluorotetralin (4),[11] was identified by [19]F n.m.r. spectroscopy and oxidation to octafluoroadipic acid.

Fluorination products (wt. % in crude mixture) from naphthalene, tetralin, and decalin

Substrate	(1)	(4)	Naphthalene	Tetralin	Decalin	Others
Naphthalene	63	27	10			
Tetralin	50	31	3	6		8
Decalin	56	29	2		4	7

The presence of naphthalene in all three fluorination mixtures suggests that the hydro-derivatives undergo dehydrogenation before fluorination. Similar sugges-

[1] Part 3, R. G. Plevey, R. W. Rendell, and M. P. Steward, J. Fluorine Chem., 1973–4, 3, 267.

[2] R. N. Haszeldine and F. Smith, J. Chem. Soc., 1950, 3617.

[3] A. K. Barbour, G. B. Barlow, and J. C. Tatlow, J. Appl. Chem., 1952, 2, 127.

[4] B. J. K. Smith and C. R. Patrick, Proc. Chem. Soc., 1961, 138.

[5] P. L. Coe, R. M. Habib, and J. C. Tatlow, unpublished results.

[6] P. L. Coe, R. G. Plevey, and J. C. Tatlow, J. Chem. Soc. (C), 1969, 1060.

[7] P. L. Coe, R. M. Habib, and J. C. Tatlow, J. Fluorine Chem., 1975, 5, 19.

[8] A. J. Edwards, R. G. Plevey, I. J. Sallomi, and J. C. Tatlow, J.C.S. Chem. Comm., 1972, 1028.

[9] M. Stacey and J. C. Tatlow, Adv. Fluorine Chem., 1960, 1, 166.

[10] J. Riera and R. Stephens, Tetrahedron, 1966, 22, 2555.

[11] B. Gething, C. R. Patrick, and J. C. Tatlow, J. Chem. Soc., 1962, 186.

tions have been made before,[9,12] and the mechanism of fluorination based [12] on oxidation of the hydrocarbon arene may be invoked.

If the oxidation theory is applied to the fluorination of naphthalene by caesium tetrafluorocobaltate(III), a sequence similar to that postulated [7] for the potassium tetrafluorocobaltate(III) is presumably involved. The products of the fluorination over the caesium salt are then explained by sequential substitution of hydrogen with fluorine leading finally to octafluoronaphthalene; further addition of fluorine must then occur readily under the conditions of the reaction.[10]

The present fluorination of naphthalene, tetralin, or decalin provides an efficient alternative route to hexadecafluorobicyclo[4.4.0]dec-1(6)-ene (1), an example of a fluoroalkene having no vinylic fluorine atoms. Recently Stephens et al.[13] have shown that compound (1), in common with all other fluoroalkenes,[14] reacts readily with simple nucleophiles. The formation of the products was rationalised as a sequence of simple addition–elimination processes, as established for other cases.[15] Fluoroalkenes are oxidised readily with solutions of potassium permanganate in acetone [16] to ketones and/or carboxylic acids. The expected product of such an oxidation of compound (1) would be the ketone (5), or its monohydration product (6), which it was hoped would


(5)   (6)   (7)
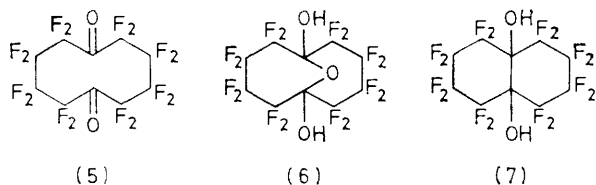
be useful precursors of fluoro-derivatives of cyclodecane. Perfluoro-ketones form hydrates readily, and models suggest that the stereochemistry of (5) is ideal for the formation of an oxygen-bridged hydrate (6). This idea is supported by conformational studies of cyclodecane-1,6-dione.[17]

With potassium permanganate in acetone, compound (1) afforded an acidic solid hydroxy-compound,[18] shown to be cis-hexadecafluorobicyclo[4.4.0]decane-1,6-diol(7) by the reactions described later. This assignment was confirmed by a single crystal X-ray structure determination.[19] The crystal structure data show the presence of considerable non-bonded interaction between fluorine atoms [2-,4-,7-, and 9-(axial) substituents]. creating strain within the molecule. The resistance to further oxidation to the ketone (5) is, therefore, unexpected but of some value since this diol cannot be

made by the methods adopted for perfluoropinacol synthesis.[20]

The diol (7) is a white crystalline solid, unchanged by prolonged boiling with solutions of potassium permanganate in acetone or water, by heating with phosphorus pentaoxide, or by treatment with ethereal lithium aluminium hydride. It is sparingly soluble in water but readily dissolves in aqueous ethanol to give acidic solutions; titration with 0.1M-sodium hydroxide gave an end-point equivalent to the formation of a dianion. However, attempts to isolate a dipotassium or barium salt were unsuccessful; fluoride ion was detected in the reaction solutions and the products gave unexpectedly

(8)   (9)
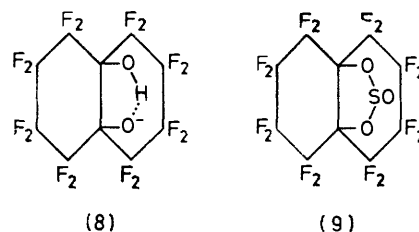
low fluorine analyses. The monopotassium salt was obtained from an aqueous solution of (7) and potassium carbonate (cf. perfluoropinacol [21]); this salt is soluble in ether. The stability of this monoalkoxide ion (8) is probably due to a strong intramolecular hydrogen bond.

Attempts at methylation of the diol (7) by the usual nucleophilic displacement-type reactions involving methyl iodide and various base–solvent systems were unsuccessful, emphasising the poor nucleophilicity of the anion. The diol was methylated with diazomethane to give the dimethyl ether and was also benzoylated without difficulty to give a diester.

A ready chlorination reaction occurs between hydrocarbon alcohols and thionyl chloride, but perfluoroalcohols cannot be chlorinated by this reagent.[21] A reaction occurs to give an intermediate, but the C–O bond is not weakened sufficiently to be cleaved by the chlorinating species. Likewise the diol (7) reacted with thionyl chloride to give a cyclic sulphite (9), which was reconverted easily by hydroxylic solvents into the diol. Pyrolysis of the sulphite (9) at 450 °C in the presence of alumina gave the alkene (1). This provides clear evidence that the product from the oxidation of the alkene (1) is the cis-diol (7) and not a hydrated form of the ketone (5).

The [19]F n.m.r. spectrum of the diol (7) is temperature-dependent [18] as are those of its derivatives. Normally AB signals would be expected, arising from the CF_2

[12] J. Burdon, I. W. Parsons, and J. C. Tatlow, Tetrahedron, 1972, 28, 43.

[13] J. A. Oliver, R. Stephens, J. C. Tatlow, and J. R. Taylor, J. Fluorine Chem., 1976, 7, 555.

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

[15] A. B. Clayton, J. Roylance, D. R. Sayers, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 1965, 7358.

[16] J. Burdon and J. C. Tatlow, J. Appl. Chem., 1958, 8, 293.

[17] T. Alvik, G. Borgen, and J. Dale, Acta Chem. Scand., 1972, 26, 1805; F. A. L. Anet, M. St. Jaques, P. M. Henrichs, A. K. Cheng, J. Krane, and L. Wong, Tetrahedron, 1974, 30, 1629.

[18] J. R. Taylor, M.Sc. Thesis, University of Birmingham, 1967.

[19] M. J. Hamor and T. A. Hamor, J.C.S. Perkin II, 1976, 383.

[20] M. Allan, A. F. Janzen, and C. J. Willis, Canad. J. Chem., 1968, 46, 3671.

[21] M. Allan, A. F. Janzen, and C. J. Willis, J.C.S. Chem. Comm., 1968, 55.

groups α and β to the ring junctions. At high temperatures the spectrum of the diol (7) comprises two AB signals, but the position is less clear for the other compounds. Sometimes an AB signal is observable, accompanied by a broad singlet (degenerate AB?) of intensity equal to that of the AB signal. As the temperature is lowered the signals broaden and then complex patterns of lines emerge; other AB signals are distinguishable. These effects, presumably associated with the adoption of certain favoured conformations of the molecules, will be reported in detail elsewhere.

EXPERIMENTAL

^{19}F N.m.r. spectra were measured on a Perkin-Elmer R10 spectrometer (56.4 MHz) for solutions in carbon tetrachloride or dimethylformamide (80 °C). Negative δ values are to high field of trichlorofluoromethane (internal reference).

Fluorination Apparatus.—Fluorinations were carried out in reactors similar to those described previously [9] containing caesium tetrafluorocobaltate(III) at 350—380 °C. The products were separated by g.l.c. on a copper column (4.6 m × 35 mm) packed with Ucon fluid 50-HB-2 000 on Chromosorb P (1 : 10) at 140 °C (N$_2$ carrier gas at 16 l h^{-1}).

Fluorination of Naphthalene, Tetralin, and Decalin.—Portions of naphthalene (4 g) were sublimed into the reactor at 350 °C over *ca.* 20 min in a stream of nitrogen at 1 l h^{-1}. The products (6.8—7.3 g), which were collected in traps cooled in liquid air, were washed with water and aqueous sodium hydrogen carbonate and dried (MgSO$_4$).

Similarly tetralin (4 g) and decalin (5 g) at 350—380 °C gave the corresponding products (5.9—6.4 and 7.0—7.2 g, respectively).

Separation and Identification of Products.—(a) *Naphthalene.* The product (5.6 g) was separated by g.l.c. to give (i) hexadecafluorobicyclo[4.4.0]dec-1(6)-ene (1) (1.7 g), b.p. 126°, ^{19}F δ −111.3(s) and −135.3(s) (1 : 1), identified by i.r. spectroscopy; [18] (ii) dodecafluorotetralin [11] (4) (0.7 g) (Found: C, 34.7. Calc. for C$_{10}$F$_{12}$: C, 34.5%), ^{19}F δ −106.9(m), −136.1 (s + m), and −145.2(m) (2 : 3 : 1), further characterised by oxidation of a sample (0.5 g) with potassium permanganate in acetone [16] to give dianilinium octafluoroadipate (0.3 g), m.p. 208—210°, identified by comparison (i.r. and ^{19}F n.m.r. spectra) with an authentic sample; and (iii) naphthalene (0.23 g).

(b) *Tetralin.* The product (6.5 g) gave (i) compound (1) (2.7 g), (ii) compound (4) (1.6 g), (iii) tetralin (0.35 g), (iv) naphthalene (0.15 g), and a mixture (0.2 g).

(c) *Decalin.* The product (5.6 g) gave compounds (1) (2.3 g) and (4) (1.2 g), decalin (0.19 g), naphthalene (0.07 g), and a mixture (0.38 g).

Oxidation of Hexadecafluorobicyclo[4.4.0]dec-1(6)-ene (1).—Compound (1) (25.7 g) was added dropwise to a stirred solution of potassium permanganate (11 g) in dry acetone (1 l). After 3/4 h at 25 °C, water (300 cm^3) was added and the acetone distilled off under reduced pressure. The residue was decolourised with sulphur dioxide and the oil

which separated was extracted with ether (3 × 100 cm^3). The dried (MgSO$_4$) extract was evaporated and the residue sublimed at 100 °C (0.1 mmHg) to give a white crystalline solid, *hexadecafluorobicyclo[4.4.0]decane-1,6-diol* (7) (21.5 g, 74.8%), m.p. 79—82° (Found: C, 26.4; H, 0.5; F, 66..3 C$_{10}$H$_2$F$_{16}$O$_2$ requires C, 26.2; H, 0.5; F, 66.4%), ν$_{max.}$ 3 350 cm^{-1} (OH), *m/e* (*M*$^+$ not detected) 439 (*M* − F), 438 (*M* − HF), and 418 (*M* − 2HF), ^{19}F δ (80 °C) −116.9 and −121.7 (AB, *J* 285 Hz), and −128.3 and −130.6 (AB, *J* 282 Hz) (1 : 1).

Evaporation of an aqueous solution of (7) neutralised with potassium carbonate solution gave the *monopotassium salt* (Found: C, 24.4; H, 0.4; F, 61.0. C$_{10}$HF$_{16}$KO$_2$ requires C, 24.2; H, 0.2; F, 61.3%), which was ether-soluble.

Reactions of the Diol (7).—(a) *Methylation.* An excess of ethereal diazomethane (from *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide) was added to the diol (2 g) in dry ether. After 12 h, evaporation left a residue which sublimed *in vacuo* to give 1,6-*dimethoxyhexadecafluorobicyclo[4.4.0]decane* (1.7 g), m.p. 55—58° (Found: C, 29.4; H, 1.0; F, 62.8. C$_{12}$H$_6$F$_{16}$O$_2$ requires C, 29.6; H, 1.2; F, 62.5%), ν$_{max.}$ 2 940 and 2 990 cm^{-1} (OCH$_3$), *m/e* (*M*$^+$ not detected) 467 (*M* − F) and 286 (*M* − C$_4$F$_8$), τ 6.15 (s, OCH$_3$), ^{19}F δ (80 °C) −114(s) and −129.5(s) (1 : 1) [at higher resolution and at 150 °C (no reference) two AB systems, *J* 280—285 and 300—305 Hz].

(b) *Benzoylation.* The diol (0.8 g), benzoyl chloride (3 cm^3), and pyridine (6 cm^3) were heated under reflux for 3/4 h. Saturated aqueous sodium hydrogen carbonate (75 cm^3) was added to the cooled mixture; the precipitate was filtered off and recrystallised (ethanol) to give the *dibenzoate* (0.5 g), m.p. 184—186° (Found: C, 43.0; H, 1.6; F, 45.3. C$_{24}$H$_{10}$F$_{16}$O$_4$ requires C, 43.3; H, 1.5; F, 45.6%), ν$_{max.}$ 1 745 cm^{-1} (C=O), τ 2.5 (m), ^{19}F δ (18 °C) −111.1 and −118.1 (AB, *J* 296 Hz), and −131.9(s) (1 : 1).

(c) *Reaction with thionyl chloride.* The diol (1.5 g) and thionyl chloride (in excess) were heated together under reflux for 72 h. The excess of thionyl chloride was evaporated off and the residue distilled *in vacuo* to give *hexadecafluorobicyclo[4.4.0]decane-1,6-diyl sulphite* (9) (1.0 g), m.p. 44—47° (Found: C, 24.1; H, 0.2; F, 60.1. C$_{10}$F$_{16}$O$_3$S requires C, 23.8; H, 0.0; F, 60.3%), ^{19}F δ (18 °C) −110.0 and −120.6 (AB, *J* 307 Hz), and −131.5 (1 : 1).

The sulphite (9) (0.5 g) decomposed on dissolution in ethanol to give, after evaporation and sublimation the diol (7) (0.36 g), i.r. spectrum identical with that of an authentic sample.

The sulphite (9) (1 g) was unchanged after heating at 180 °C for 3 h. However when it (0.9 g) was passed in a stream of nitrogen (2 l h^{-1}) through a glass tube (30 cm × 25 mm) packed with fused alumina granules (antibumping granules) at 450 °C and the product was collected in a liquid-air cooled trap and distilled *in vacuo*, the olefin (1) (0.5 g), identified by i.r. spectroscopy, was obtained.