

Polyfluoro-compounds based on the cycloheptane ring system Part 9. Further products derived from dodecafluorocycloheptane

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Abstract

Dodecafluorocycloheptene (II) reacted by addition/elimination with *n*-BuOH/KOH, *n*-BuLi, *n*-BuMgBr and MeO(CH₂)₃MgBr to give undecafluorocycloheptenes with the appropriate nucleophilic group in the 1-position, or decafluorocycloheptenes with such groups in the 1,2-positions. 1-[I(CH₂)₃]-C₇F₁₁ was made from the analogous methoxy-compound and cyclized to the decafluorobicyclo-[5,3,0]dec-1(7)-ene. Reactions of II with NaBH₄ and with LiAlH₄ afforded 1H-undeca-, 1H,2H-deca- (XIII), and 1H,7H,7H-nona-fluorocycloheptene. Diels–Alder cyclo-additions of cyclopentadiene to fluorocycloheptenes II and XIII gave appropriate tricyclo-adducts. The structures of all products were confirmed spectroscopically. © 1997 Elsevier Science S.A.

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1. Introduction

Various investigations into polyfluorinated derivatives of cycloheptane have been reported [1]. Included among the range of compounds made were certain polyfluorobicyclic compounds incorporating seven-membered rings—[3,2,0]-heptanes and [3,2,2]nonanes [2,3]. The present work describes further syntheses starting from dodecafluorocycloheptene (II) [4], and it was hoped that one outcome might be to provide a route to polyfluorobicyclo[5,3,0]decanes. These are of special interest, being possible precursors of polyfluoroazulenes. They are also examples of a fluorobicyclic system of a new type, permitting further study of the acidity of bridgehead hydrogen at a fused-ring position (cf. [5]). Though neither of these ultimate objectives was realized, some new compounds were made and are now reported.

2. Results and discussion

Dodecafluorocycloheptene (II) was obtained [4] by dehydrofluorination (aqueous KOH) of tridecafluorocyclohep-

tane (I), which was a major constituent of the mixture resulting from fluorination of cycloheptane by cobalt trifluoride at 180–200 °C [4,6]. We also used an identical fluorination process with cyclohepta-1,3,5-triene, which gave very similar results, but afforded rather higher proportions of I.

Dehydrofluorination of I by aqueous KOH was found to be less difficult than had been believed originally [4]: with care it could be carried out on a fairly large scale under standard conditions.

Earlier work had shown that the vinylic fluorines of dodecafluorocycloheptene (II) were replaced readily by –Me, –H, and –OMe, via attack by nucleophilic reagents, respectively, methyl lithium [7], lithium aluminium hydride [4] or sodium borohydride [7], and methanolic potassium hydroxide [4]. These processes are normally regarded as addition/elimination sequences and are typical of the reactivity shown by polyfluorocycloalkenes (cf. [5,8]).

Fig. 1.

Attempts were made to utilize similar reactions to synthesize intermediates via which a three-carbon unit could be bridged across the 1,2-double bond positions of II (i.e. to give a fused five-membered ring). Firstly, nucleophilic addition/elimination by the mono-lithium derivative of 1,3-dibromopropane was tried, but a complex mixture resulted, not surprisingly in retrospect. To characterize one product thought to be formed (the lithium source was *n*-butyllithium), a reaction of the latter with II was carried out at

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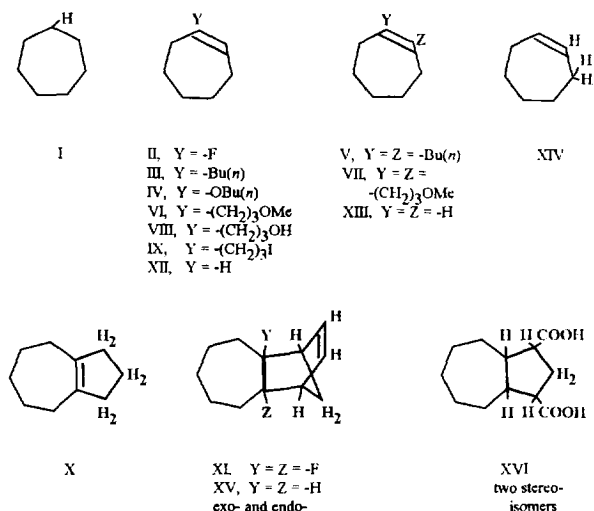


Fig. 1. All unmarked bonds are to fluorine.

–78 °C, to give the expected 1-*n*-butylundecafluorocycloheptene (III).

Next, 1-bromo-3-methoxypropane was lithiated by exchange with *n*-butyllithium, and the mixture added to II at –20 °C. The only product recognized was 1-*n*-butoxyundecafluorocycloheptene (IV), which must have arisen via the ingress of oxygen or moisture into the reaction system. An authentic sample of IV was made by reaction of II with *n*-butanol/potassium hydroxide.

Since reactions with suitable lithiates were difficult, Grignard reagents were used, since they also give addition/elimination products with fluoro-olefins [9]. *n*-Butylmagnesium bromide was generated in tetrahydrofuran, and, in the refluxing solvent, converted a deficiency of II into 1,2-di(*n*-butyl)decafluorocycloheptene (V).

Under similar conditions, when an equimolar amount of II was added to 3-methoxypropylmagnesium bromide, two products were obtained, 1-(3'-methoxypropyl)undecafluorocycloheptene (VI) and 1,2-di(3'-methoxypropyl)decafluorocycloheptene (VII). Reverse addition afforded a higher proportion of VI. Of the standard reagents for cleavage of ethers, only hydriodic acid was successful with VI. Refluxing with a 15 molar excess gave 1-(3'-hydroxypropyl)undecafluorocycloheptene (VIII) and 1-(3'-iodopropyl)undecafluorocycloheptene (IX); use of a 25 molar excess afforded IX exclusively.

Unexpectedly, compounds VIII and IX were unreactive (fluoroalkyl units do not normally influence reactivity greatly when the functional group is at the remote end of an *n*-propyl chain). Cyclization of VIII using basic reagents could not be accomplished, and neither could conversions of IX to VIII or to the propenyl derivative. Further, it was not found possible to generate lithium or magnesium derivatives from IX under controlled conditions; if reactions were forced, tarry residues resulted.

Cyclization of IX was finally achieved using lithium amalgam in diethyl ether, though yields and conversions were very poor. The product was identified as the desired

2,2,3,3,4,4,5,5,6,6-decafluorobicyclo[5,3,0]dec-1(7)-ene (X). However, the overall process from II to form this bicyclic system was not sufficiently viable to merit extending the work.

The possibility was next examined of using Diels–Alder reactions [10] of fluorocycloheptenes to generate precursors potentially capable of conversion to derivatives of this bicyclic system. Cyclopentadiene and II reacted smoothly at 100 °C, to give the tricyclic compound XI (exo- and endo-forms). However, attempts at oxidation of the double bond of XI, to form the required bicyclic system, caused deep-seated decomposition. The only product to be identified was decafluoropimelic acid [4]. Presumably, concomitantly with double bond breakage, the tertiary fluorines were lost by dehydrofluorination, and all the rings were then degraded.

An analogue of XI with no tertiary fluorines was then made. 1H-Undeca- (XII) and 1H,2H-deca-fluorocycloheptene (XIII) were known [7], via the action of sodium borohydride on II. Higher proportions of the desired product, XIII, were obtained using an increased ratio of borohydride, but a further product, 1H,7H,7H-nonafluorocycloheptene (XIV) was also formed. Use of an excess of lithium aluminium hydride afforded some XIII, but mostly XIV.

The reaction pathway is a simplified version of that followed by decafluorocyclohexene [11]. In the present case, no isomers of XII and XIII were detected which arose by ‘‘outwards elimination’’, ie regeneration of the double bond by loss of F from an original allylic position (cf. [5,8]). The trihydro-compound XIV can of course only arise from XIII by loss of an F from a position originally allylic. Presumably, the predominant formation of XII and XIII arises because of the low stereochemical demands in eliminations in the polyfluorocycloheptane series (cf. [5]). It was fortunate therefore that, in similar sequences on decafluorocyclohepta-1,3- and -1,4-dienes, some products did arise by regeneration of unsaturation via ‘‘outwards elimination’’, thus making possible the first syntheses of octafluorocyclohepta-1,3,5-triene and thence perfluorotropone [12].

Cyclopentadiene reacted readily with the 1H,2H-ene (XIII) to give the tricyclic compound XV (exo- and endo-forms). Oxidation of the double bond of XV was achieved by sodium permanganate in a heterogeneous system [13], but the derived dicarboxylic acid (XVI; two stereoisomers present) was not very stable, and gradually decomposed during purification. Controlled decarboxylation could not be accomplished by use of any of the standard processes. Again, the sequence from II was not sufficiently attractive to justify continuation of the project.

3. Experimental details

3.1. General

3.1.1. Gas–liquid chromatography

Small-scale preparative GLC separations were carried out in Pye 104 or 105 machines, using 9 m × 10 mm tubes having the following packings: A, Ucon oil (LB 550X)/Chromo-

sorb P30-60 (1:4); B, silicone gum (si 301)/Universal B (1:9); C, silicone gum (Si 301)/Celite (1:9). For larger-scale separations, copper tubes were used (katharometer detectors): column D, 4.8 m × 35 mm; packing, Ucon oil (50-HB-2000)/Chromosorb P (1:9): column E, 4.8 m × 75 mm; packing, dinonyl phthalate/Chromosorb P (1:5). For each separation, the unit used, temperature (°C), and nitrogen carrier gas flow rate (1 h⁻¹) are given.

3.1.2. Spectroscopy

Spectral data were measured as described in Part 8 [1]. ¹H NMR chemical shifts are recorded to low field of tetramethylsilane, ¹⁹F shifts to high field of trichlorofluoromethane. Quoted for each peak are, respectively, the position assigned to the parent atom in the formula, the intensity (in brackets), the chemical shift, the signal form and the coupling constants (in Hz). Peak positions corresponded closely with those of related compounds [4,7,14]. Infrared (IR) spectra were done on liquid films.

3.2. Dodecafluorocycloheptene (II) from tridecafluorocycloheptane (I)

The latter (250 g) was refluxed gently with potassium hydroxide (160 g) in water (400 cm³) for 15 h. Water (400 cm³) was added, the lower layer separated, washed, dried and distilled (30 cm column) to give II (212 g) with similar characteristics to those reported before [4].

3.3. 1-*n*-Butylundecafluorocycloheptene (III)

n-Butyllithium in hexane (17 cm³, 2M) mixed with dry diethyl ether (25 cm³) were added dropwise to a stirred solution of II (11.6 g) in ether (25 cm³), held at -78 °C, during 1 h. After further stirring (1 h at -78 °C, 12 h at 15 °C) sulphuric acid (15 cm³, 2M) was added carefully and the ether layer separated, washed and dried. The most volatile components were distilled off through a short column, and the residue (8.8 g) separated by GLC (D, 80, 15). Isolated were: (i) and (ii), unknowns (0.9 g each); (iii), III (4.0 g); (iv), unknown (1.7 g). III had b.p. 150 °C (Found: C, 37.9; H, 2.8; F, 60.0. C₁₁H₉F₁₁ requires C, 37.7; H, 2.6; F, 59.7%): *M/e* 350 (M): IR 1690 (-CF=C<): NMR (in CCl₄), ¹⁹F; 2, (1) 113.7; 3, (2) 115.5; 4 and 6, (4) 128.9; 5, (2) 130.9; 7, (2) 107.8; all broad: ¹H; 1', (2) 2.50 b; 2' and 3', (4) 1.45 c; 4', (3) 1.04 t, *J*_{4,3'} = 6.5.

3.4. 1-*n*-Butoxyundecafluorocycloheptene (IV)

A solution of potassium hydroxide (0.80 g) in *n*-butanol (0.76 g) was added to II (3.12 g) at 15 °C. When the initial reaction had subsided, the mixture was stirred for 90 min at 15 °C. Water was added and the lower layer washed, dried and distilled to give IV (2.35 g). A pure sample (by GLC; A, 130, 4) had b.p. 174–176 °C (Found: C, 35.9; H, 2.6; F, 56.9. C₁₁H₉F₁₁O requires C, 36.1; H, 2.5; F, 57.1%): *M/e*

351 (M-CH₃): IR 1685 (-CF=C<): NMR (in CCl₄), ¹⁹F; 2, (1) 142.7; 3 and 7, (2) 113.4, (2) 114.8; 4, 5 and 6, (2) 128.7, (2) 129.8, (2) 130.7; all b: ¹H; 1', (2) 4.18 dt, *J*_{1,2} = 2.0, *J*_{1,2'} = 6.5; 2' and 3', (4) 1.65 cq, *J*_{3,4'} = 6.4; 4', (3) 1.00 t, *J*_{4,3'} = 6.4.

3.5. 1,2-*di-n*-Butyldecafluorocycloheptene (V)

A solution of *n*-butyl bromide (13.7 g) in tetrahydrofuran (THF; 15 cm³; freshly distilled from calcium hydride, as for all such reactions) was added to magnesium turnings (2.4 g) in THF (50 cm³), with stirring, to maintain a gentle reflux. The mixture was stirred for 1 h at 15 °C, and II (9.4 g) then added dropwise to maintain a gentle reflux; on completion, refluxing was continued for 1 h. After being quenched with dilute hydrochloric acid and washed with water, the fluorocarbon layer was dried and the most volatile fractions distilled off. Distillation in vacuo gave a liquid (8.5 g); of this, part (4.8 g) was separated by GLC (B, 150, 3), affording V (2.9 g), b.p. 235–236 °C (Found: C, 46.2; H, 4.8; F, 48.7. C₁₅H₁₈F₁₀ requires C, 46.4; H, 4.7; F, 48.9%): *M/e* 388 (M): IR 1640 (vw, >C=C<): NMR (in CCl₄), ¹⁹F; 3 and 7 (2) 105.4; 4, 5 and 6, (3) 128.5; both b: ¹H; 1' and 1'' (2) 2.40 b; 2', 2'', 3' and 3'' (4) 1.45 c; 4' and 4'', (3) 1.04 t, *J*_{4,3'} = *J*_{4'',3''} = 5.1.

3.6. 1-(3'-Methoxypropyl)undecafluorocycloheptene (VI) and 1,2-di(3' methoxypropyl)decafluorocycloheptene (VII)

A solution of 1-bromo-3-methoxypropane [15] (4.6 g) in THF (15 cm³) was added to magnesium turnings (0.7 g) in THF (50 cm³), with stirring, to maintain a gentle reflux. II (9.3 g) was then added dropwise and the mixture refluxed for 30 min. After being quenched with dilute hydrochloric acid and washed with water, the fluorocarbon layer was dried and the most volatile fractions distilled off. Distillation in vacuo gave a liquid (3.9 g), which was separated by GLC (C, 120, 3.6), affording (i), THF, II and 1-bromo-3-methoxypropane (1.2 g in all): (ii), VI (1.1 g); (iii), VII (0.2 g). VI had b.p. 178–180 °C (Found: C, 36.2; H, 2.7; F, 57.3. C₁₁H₉F₁₁O requires C, 36.1; H, 2.5; F, 57.1%): *M/e* 366 (M): IR 1690 (-CF=C<): NMR (in CCl₄), ¹⁹F; 2, (1) 112.7; 3, (2) 115.3; 4 and 6, (4) 127.2; 5, (2) 129.3; 7, (2) 107.5; all b: ¹H; 1', (2) 2.57 b; 2', (2) 1.77 c; 3' and 5' (5) 3.35 c. VII had b.p. 271–273 °C (Found: C, 42.8; H, 4.0; F, 45.1. C₁₅H₁₈F₁₀O₂ requires C, 42.9; H, 4.3; F, 45.2%): IR 1640 (vw, >C=C<): NMR (in CDCl₃), ¹⁹F; 3 and 7 (2) 104.9; 4, 5 and 6, (3) 128.3; both b: ¹H; 1' and 1'' (2) 2.57; 2' and 2'', (2) 1.77; 3', 3'' 5' and 5'', (5) 3.35; all c.

1-Bromo-3-methoxypropane (27.0 g) was added to magnesium turnings (4.2 g) in THF (100 cm³), with stirring, to maintain a gentle reflux. The mixture was then added dropwise during 15 min. to a stirred solution of II (55.0 g) in THF (250 cm³) at 15 °C. After being refluxed for 2 h, the usual work-up followed. The residue (48.8 g) was distilled in vacuo to give (i), THF and II (9.0 g): (ii), VI (27.7 g)

b.p. 33–42 °C/0.25 mm: (iii), impure VI (1.6 g); (iv), residue, (6.2 g).

3.7. 1-(3'-Hydroxypropyl)undecafluorocycloheptene (VIII) and 1-(3'-iodopropyl)undecafluorocycloheptene (IX)

Compound VI (11.8 g) was refluxed with hydriodic acid (40 cm³; s.g. 1.7) for 3 h. After addition of water, the fluorocarbon layer was separated, washed (including with sodium metabisulphite solution), and dried (11.3 g). Separation by GLC (B, 120, 3.6) of a portion (1.7 g) gave VIII (0.3 g) and IX (0.42 g). VII had b.p. 204–205 °C (Found: C, 34.4; H, 2.2. C₁₀H₇F₁₁O requires C, 34.1; H, 2.0%); IR 1685 (–CF=C<): NMR (in CDCl₃), ¹⁹F; 2, (1) 111.3; 3, (2) 114.1; 4 and 6, (4) 127.5; 5, (2) 129.6; 7, (2) 106.1; all b: ¹H; 1', (2) 2.50 b; 2', (2) 1.75 c; 3', (2) 3.67 t, J_{3,2'} = 6.0; –OH, (1) 1.57 s.

IX had b.p. 220–223 °C (Found: C, 26.1; H, 1.6; F, 45.1. C₁₀H₆F₁₁I requires C, 26.0; H, 1.3; F, 45.2%): M/e 462 (M), 335 (M–I); IR 1690 (–CF=C<): NMR (in CDCl₃), ¹⁹F; 2, (1) 109.8; 3, (2) 114.0; 4 and 6, (4) 127.5; 5, (2) 129.7; 7, (2) 106.0; all b: ¹H; 1', (1) 2.60 b; 2', (1) 2.05 c; 3', (1) 3.17 t, J_{3,2'} = 6.3.

Compound VI (9.3 g) was refluxed with hydriodic acid (50 cm³; s.g. 1.7) for 3 h. After isolation as before, IX (9.0 g), was obtained.

3.8. 2,2,3,3,4,4,5,5,6,6-Decafluorobicyclo[5,3,0]dec-1(7)-ene (X)

A solution of IX (9.6 g) in dry diethyl ether (30 cm³) was added dropwise to lithium amalgam (Li, 0.45 g; Hg 200 g) in ether (20 cm³) in a nitrogen atmosphere, and the mixture stirred for 5 h at 15 °C. After addition of dilute sulphuric acid, filtration, extraction with ether separation and drying, ether was distilled off. Further distillation at 22 mm pressure gave (i), (1.47 g), b.p. up to 116 °C; (ii), IX (0.65 g), b.p. 116–130 °C; (iii), residue (0.9 g). GLC separation (B, 150, 4.0) of (i) afforded X (0.10 g) and IX (0.90 g). X had b.p. 195–196 °C, m.p. 27–28 °C (Found: M/e 316.029395. C₁₀H₆F₁₀ requires M, 316.030970): IR 1675 (w, >C=C<): NMR (in CCl₄), ¹⁹F; 2 and 6, (2) 108.0; 3 and 5, (2) 129.1; 4, (1) 127.2; all b: ¹H; 8 and 10, (2) 2.87 b; 9, (1) 2.00 p, J_{9,8}, J_{9,10} = 6.6.

3.9. 2,3,3,4,4,5,5,6,6,7,7,8-Decafluorotricyclo[7,2,1,0^{2,8}]dodec-1-ene (XI) from dodecafluorocycloheptene (II)

Freshly distilled cyclopentadiene (1.4 g) and II (6.3 g) were shaken together in a sealed Pyrex glass tube (25 × 2 cm) for 24 h at 100 °C. Distillation (65 °C; 0.5 mm) gave exo- and endo-isomers of XI (4.9 g), b.p. 214 °C (Found: C, 38.3; H, 1.8; F, 60.6. C₁₂H₆F₁₂ requires C, 38.1; H, 1.6; F, 60.3%): M/e 378 (M): NMR (in CDCl₃), ¹⁹F; 2 and 8 (2) 161.7, (2) 163.4, both d, J = 39.5; 3–7, peaks (overlapping AB s)

centred at (2) 115.1; (8) 119.0; (5) 124.0; (3) 129.5; (1) 132.7; (1) 134.8; (<1) 137.8; all b (intensities approximate): ¹H; 1 and 9, (1) 3.35, (1) 3.57, both c; 10 and 11, (1) 6.15 b, (1) 6.41 t, J = 1.87; 12, (2) 2.17.

Attempted oxidation of XI by the method used below for compound XV gave only a brown resin; potassium permanganate in dilute sulphuric acid afforded decafluoropimelic acid, isolated as its bis-S-benzylthiuronium salt [4].

3.10. 1H-Undecafluorocycloheptene (XII), 1H,2H-decafluorocycloheptene (XIII) and 1H,7H,7H-nonafluorocycloheptene (XIV)

A suspension of sodium borohydride (6.0 g) in dry diglyme (200 cm³) was added dropwise over 1 h to stirred II (55.0 g) in diglyme (50 cm³) at 0 °C, and stirring was continued at 0 °C for 2 h further. Dilute sulphuric acid was added slowly and the lower layer (40.0 g) separated, washed, and dried. Distillation in vacuo gave a liquid (30.0 g), which by GLC separation (E, 90, 75), afforded (i), a mixture of II and XII [4] (10.6 g); (ii), XIII [7] (10.1 g); (iii), XIV, (3.1 g). XIV had b.p. 124–125 °C (Found: C, 32.2; H, 1.4; F, 65.9. C₇H₃F₉ requires C, 32.6; H, 1.2; F, 66.2%): M/e 258 (M): IR 1710 (–CF=CH–): NMR (in CCl₄), ¹⁹F; 2, (1) 116.1; 3 and 6, (2) 112.2, (2) 119.1; 4 and 5, (4) 130.9; all c: ¹H; 1, (1) 5.79 dt, J_{1,2} = 8.0, J_{1,7} = 8.0; 7, (2), 2.92 dt, J_{7,1} = 8.0, J_{7,6} = 12.0

A suspension of lithium aluminum hydride (1.52 g) in dry ether (50 cm³) was added dropwise over 30 min to stirred II (6.24 g) in ether (30 cm³) at 0 °C, and the mixture was then refluxed for 11 h. Wet ether, water and dilute sulphuric acid were successively added cautiously and the ether layer separated, washed, and dried. Distillation through a short column left a residue (6.9 g), which by GLC separation (A, 130, 3.6), afforded (i), XIII [7] (0.72 g); (ii), XIV (1.92 g).

3.11. 3,3,4,4,5,5,6,6,7,7-Decafluorotricyclo[7,2,1,0^{2,8}]dodec-10-ene (XV) from 1H,2H-decafluorocycloheptene (XIII)

Freshly distilled cyclopentadiene (1.3 g) and XIII (5.5 g) were shaken together in a sealed Pyrex glass tube (25 × 2 cm) for 24 h at 100 °C. Distillation of the product (60 °C; 0.4 mm) gave crude XV (5.3 g). Part (0.9 g) was separated by GLC (C, 120, 3.0) to give endo- and exo-isomers of XV (0.6 g), b.p. 223–224 °C (Found: F, 55.7. C₁₂H₈F₁₀ requires F, 55.5): M/e 342 (M): NMR (in CDCl₃), ¹⁹F; 3–7, peaks (overlapping AB s) centred at (1) 103.5; (3) 108.4; (2) 116.3; (1) 118.3; (3) 120.4; (1) 123.8; (3) 125.3; (4) 134.3; (2) 139.3; all b (intensities approximate): ¹H; 1 and 9, (1) 3.35 b; 2 and 8, (1) 3.00 d, J = 33; 10 and 11, (1) 6.20 c; 12, (1) 1.48 AB, J = 8.5.

3.12. 2,2,3,3,4,4,5,5,6,6-Decafluorobicyclo[5,3,0]decane-8,10-dicarboxylic acid (XVI) from the tricyclic compound XV

A solution of sodium permanganate (4.6 g) in water (30 cm³) was added dropwise during 15 min to a stirred mixture of XV (3.2 g), acetone (20 cm³), 2,2,4-trimethylpentane (20 cm³) and water (80 cm³) at 15 °C. The mixture was stirred at 15 °C for 5 h, carbon dioxide being passed through continuously to keep the pH at about 6. After passage of sulphur dioxide to dissolve manganese dioxide, the white precipitate remaining was collected (1.8 g) and recrystallized from water to give XVI (0.6 g) m.p. 208–210 °C, (Found: C, 35.6; H, 2.1; F, 46.8. C₁₂H₈F₁₀O₄ requires C, 35.5; H, 2.0; F, 46.8%): IR (Nujol mull), 3050–3150 (–OH), 1720 (>C=O): NMR (in CD₃COCD₃), ¹⁹F; 2–6, peaks (overlapping AB s) centred at (1) 107.3; (1) 111.0; (1) 116.0; (1) 118.8; (1) 120.3; (2) 123.5; (2) 133.7; (1) 138.8; all b (intensities approximate): ¹H; 1, 7, 8 and 10, (2) 3.1 c; 9 (1) 2.00 b; –COOH, (1) 8.40 b. Two stereoisomers were present.

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