

Reactions of Fluoroalkyl Radicals Generated Electrochemically. Part 2. Addition of Heptafluoropropyl Radicals to Methyl Methacrylate

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Heptafluoropropyl radicals, generated by the electrolysis of heptafluorobutyric acid, reacted with methyl methacrylate to give a mixture of products of the type $R_FCH_2CH(Me)X$, $R_FCH_2C(Me)(R_F)X$, $[R_FCH_2C(Me)X]_2$ and $R_FCH=C(Me)X$, where $R_F = C_3F_7$ and $X = CO_2Me$. Also formed by electrochemical oxidation of the product of the initial radical addition reaction were $CH_2=C(CH_2R_F)X$, $(R_FCH_2)_2CHX$, and $(R_FCH_2)_2C(R_F)X$, this being the preferred process. A trimeric and second dimeric product were also formed.

Discussion

In previous papers^{1,2} we described the reactions of trifluoromethyl radicals, generated by the electrolysis of trifluoroacetic acid, with alk-1-enes, $CH_2=CHX$, where $X =$ alkyl, CN, CO_2Me or CH_2CO_2Me . The products of the reactions resulted from initial addition of a trifluoromethyl radical to the terminal carbon atom of the alkene. Further reactions of the radical so formed, involving either addition of a second trifluoromethyl radical, hydrogen atom abstraction, dimerization, or further oxidation of the radical to a carbonium ion, then led to the identified products.

We now describe the reaction of electrolytically generated heptafluoropropyl radicals with methyl methacrylate. From the product mixture was first isolated methyl 2-(2,2,3,3,4,4,4-heptafluorobutyl)acrylate (1), identified by elemental analysis, and i.r. and n.m.r. spectroscopy. The ^{19}F n.m.r. spectrum consisted of a signal at ϕ 81.00 (t, J 10.5 Hz), ascribed to a CF_3 group, and two other signals at ϕ 114.54 and 127.78 (both m), due to two CF_2 groups, all in the correct intensity ratio. The 1H n.m.r. spectrum showed signals typical of MeO, two olefinic protons, and a methylene group, although no signal was observed at δ 1.0–1.6 suggesting the absence of a methyl group.

Also isolated was methyl 2-methyl-2-(heptafluoropropyl)-4,4,5,5,6,6,6-heptafluorohexanoate (2); the ^{19}F n.m.r. spectrum contained signals at ϕ 80.90 (t, J 10.5 Hz), 114.88, and 128.62 ascribed to the heptafluoropropyl group and further signals at ϕ 81.48 (t, J 12.4 Hz), 123.06, and an AB system δ_A 106.24, δ_B 117.32, J_{AB} 260 Hz due to a second heptafluoropropyl group attached to the chiral centre. The 1H n.m.r. and i.r. spectra were consistent with the proposed structure.

From the g.l.c. separation was obtained a second hexanoate (3). Accurate mass measurement was consistent with the molecular formula $C_{14}H_7F_{21}O_2$; the ^{19}F n.m.r. spectrum showed signals at ϕ 80.98 (t, J 10.4 Hz), 128.66, and an AB system, δ_A 107.71, δ_B 116.65, J_{AB} 267 Hz (total intensity ratio 2), together with signals at ϕ 81.40 (t, J 12.3 Hz), 110.50, and 123.40 (total intensity ratio 1). We therefore conclude that (3) contains three heptafluoropropyl groups, two in identical environments. Together with the i.r. and 1H n.m.r. spectrum this indicates that compound (3) is methyl 2-(heptafluoropropyl)-2-(2,2,3,3,4,4,4-heptafluorobutyl)-4,4,5,5,6,6,6-heptafluorohexanoate.

From this separation was also obtained a mixture of compounds in the ratio 3 : 1. Hydrogenation of the mixture gave a single component identified by chemical analysis and spectroscopy as methyl 2-methyl-4,4,5,5,6,6,6-heptafluorohexanoate (4). The ^{19}F and 1H n.m.r. signals due to (4) were all present in the n.m.r. spectra of the mixture in the correct intensity ratios, and, after subtraction of the signals due to (4), the remaining signals were consistent with (*E*)-methyl 2-

methyl-4,4,5,5,6,6,6-heptafluorohex-2-enoate (5), the assignment of the structure to the (*E*) isomer being made on the basis of the chemical shift of the olefinic proton.

From the reaction mixture was also isolated (6), identified as methyl 2-(2,2,3,3,4,4,4-heptafluorobutyl)-4,4,5,5,6,6,6-heptafluorohexanoate, with an accurate mass measurement, and i.r. and n.m.r. spectra in agreement with the structure proposed. Since mass measurement suggested the presence of two heptafluoropropyl groups, although the ^{19}F n.m.r. spectroscopy showed only one set of resonances for $C_3F_7^-$, the environment of two groups must be the same.

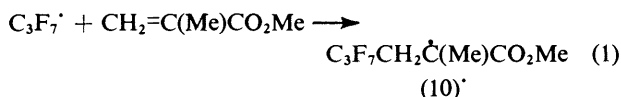
Separation by g.l.c. of the highest boiling fraction afforded, in addition to (3), dimeric and trimeric products. The first of these was identified as an equimolar mixture of (\pm)- and *meso*-dimethyl 2,3-dimethyl-2,3-bis(2,2,3,3,4,4,4-heptafluorobutyl)succinate (7). A sample gave a correct accurate mass measurement and cracking pattern together with an appropriate i.r. spectrum. The ^{19}F n.m.r. spectrum contained signals typical of two heptafluoropropyl groups of equal intensity in very similar environments. The 1H n.m.r. spectrum was also consistent with a mixture of (\pm)- and *meso*-succinates, showing two signals of equal intensity at δ 1.37 and 1.28 of total intensity ratio 3 H. Each of these signals were doublets (J 3.3 Hz), shown to be due to coupling since the line separation was unaffected by a change in spectrometer frequency. Furthermore the splitting was shown to arise by long range coupling to fluorine since the spectrum taken with fluorine spin decoupling caused the two Me doublets to collapse to singlets.

Accurate mass measurement of compound (8) gave fragments of mass 855.0470 and 843.0180, consistent with molecular formulae $C_{22}H_{14}F_{27}O_4$ and $C_{21}H_{11}F_{28}O_3$, indicating the presence of four heptafluoropropyl groups, in agreement with the ^{19}F n.m.r. spectrum which showed a complex signal at ϕ 80.66–81.22 consisting of a set of overlapping triplets due to CF_3 groups. The 1H n.m.r. spectrum showed the presence of three methoxycarbonyl groups in the ratio 2 : 1, together with one methyl group, appearing as a doublet (J 3.5 Hz) due to long range coupling to fluorine, and ten other protons, which fluorine spin decoupling caused to appear as a set of five overlapping AB systems. We therefore identify compound (8) as trimethyl 1,1,1,2,2,3,3,10,10,11,11,12,12-tetradecafluoro-5,8-bis(2,2,3,3,4,4,4-heptafluorobutyl)-7-methyl-dodecane-5,7,8-tricarboxylate, with a structure consistent with other compounds isolated from the reaction mixture and with the proposed mechanism of reaction (see later).

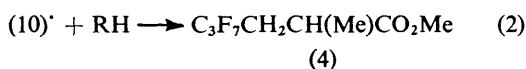
Finally compound (9) was tentatively identified as methyl 4-carboxy-6,6,7,7,8,8,8-heptafluoro-2,4-dimethyloct-2-enoate. The i.r. spectrum showed the presence of OH, $>C=O$, and $>C=C<$, and the ^{19}F n.m.r. spectrum the presence of a heptafluoropropyl group attached to a prochiral (or chiral)

centre. The ^1H n.m.r. spectrum was in agreement with the proposed structure, although the signal due to the hydroxy proton was not observed.

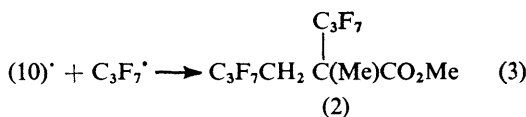
Although the number of products formed from the reaction of heptafluoropropyl radicals with methyl methacrylate is greater than that found with methyl acrylate and trifluoromethyl radicals,¹ we believe that essentially similar reaction pathways are followed in each case. Heptafluoropropyl radicals, generated by the anodic oxidation of heptafluorobutyric acid, react with the double bond at the terminal position to give the stable tertiary radical (10) \cdot [equation (1)]:



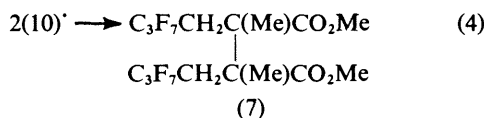
This radical may then undergo one of several reactions: (i) abstraction of a hydrogen atom from either solvent or monomer, resulting in compound (4) [equation (2)]:



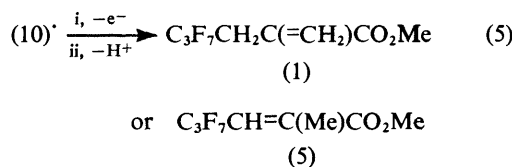
(ii) reaction with a second heptafluoropropyl radical to afford compound (2) [equation (3)]:



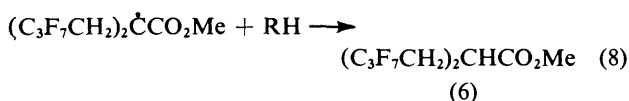
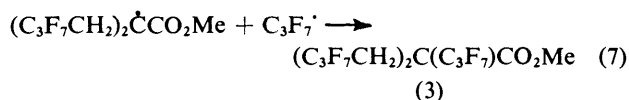
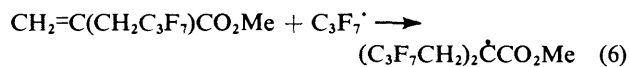
or (iii) dimerization to generate compound (7) [equation (4)]:



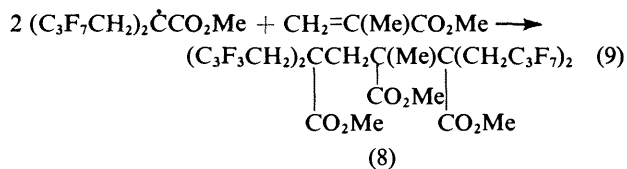
We also isolated from the reaction mixture two alkenes [(1) and (5)]. We believe these arise by the further electrochemical oxidation of the radical formed in equation (1) to a carbonium ion followed by loss of a hydrogen ion from either the methyl or methylene group, as in equation (5):



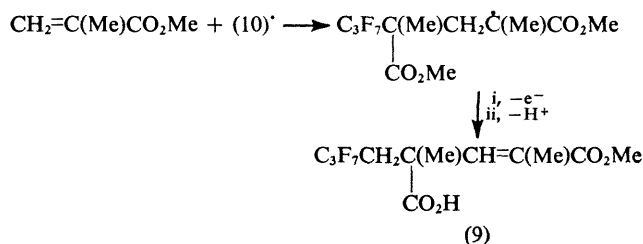
Products (3) and (6) may then plausibly be accounted for by reactions analogous to those shown in equations (1)–(3) involving the alkene (1), *viz.* the reaction in equation (6) followed by reaction with a further heptafluoropropyl radical to give compound (3) [equation (7)] or a hydrogen atom abstraction reaction resulting in (6) [equation (8)]:



The formation of compound (8) is consistent with this reaction sequence and arises from the addition of two of the radicals formed in equation (6) to methyl methacrylate [equation (9)]:



Addition of the radical (10) \cdot formed in equation (1) to methyl methacrylate, followed by electrochemical oxidation, with hydrolysis of one of the methoxycarbonyl groups occurring during separation and work-up, may then account for the formation of (9), as shown in the Scheme.



Scheme.

According to the mechanism proposed above compounds (1), (3), (5), (6), and (8) arise from various reaction sequences, all of which commence with the electrochemical oxidation of the radical formed in the reaction shown in equation (1), whereas compounds (2), (4), and (7) result from reactions in which the radical is not oxidized. After correction for g.l.c. losses, the molar ratio 2.2 : 1 may be calculated for the two groups of compounds. Thus the preferred fate of the radical formed in the reaction in equation (1) is electrochemical oxidation. This result is in contrast with our previous results where only low yields of unsaturated compounds were obtained from the reaction of trifluoromethyl radicals with alk-1-enes and methyl vinylacetate and no alkenes were isolated using methyl acrylate or acrylonitrile. The difference in behaviour between methyl methacrylate and methyl acrylate may be due to the greater ease of electrochemical oxidation of the tertiary radical arising from the former in accord with previous theoretical calculations³ and experimental results.⁴

Experimental

The electrolyses were carried out at constant current as previously described.¹ N.m.r. spectra were measured on Varian HA 100, and Perkin-Elmer R10 and R12 n.m.r. spectrometers for solutions in CCl_4 unless otherwise stated. ^1H Chemical shifts are reported in δ values (p.p.m. from tetramethylsilane) and ^{19}F shifts in ϕ values (p.p.m. from CCl_3F). ^1H and ^{19}F Spectra were run at 60 and 56.4 MHz unless otherwise stated. I.r. spectra were recorded on a Perkin-Elmer 257 i.r. spectrophotometer.

G.l.c. was carried out using a Pye 104 gas chromatograph with nitrogen as carrier gas and a flame ionization detector using the following columns and stationary phases: column A, DIDP–Chromosorb P 1 : 3; column B, Kel-F oil–Chromosorb P 1 : 10; column C, Ucon LB550X–Chromosorb P 1 : 6; column D, Carbowax–Chromosorb P 1 : 5. All columns were 9.1 m \times 7 mm i.d. Ether refers to diethyl ether.

Results.—Heptafluorobutyric acid (32.1 g) and methyl methacrylate (5.0 g) were dissolved in acetonitrile (40 cm³) and water (5.6 cm³) containing NaOH (0.3 g) and the mixture was electrolysed at 1.0 A for 4 h as previously described.¹ The reaction mixture was then poured onto water (100 cm³) and the organic layer separated. The aqueous phase was extracted with ether (4 × 60 cm³) and the ethereal extract combined with the organic layer previously separated. The combined solutions were washed with aq. NaHCO₃ (4 × 50 cm³, 8% w/v) and water (4 × 50 cm³), and dried (MgSO₄). The solution was evaporated to remove the ether, leaving a residue (16.7 g) which was distilled at 0.2 mmHg at room temperature to afford a distillate (7.1 g) and a residue (9.6 g), both mixtures.

A portion (0.65 g) of the distillate was separated by g.l.c. (column A, 137 °C, 5 l/h N₂) to afford (i) a liquid (0.051 g) shown by g.l.c. to be a mixture of ether and acetonitrile; (ii) a mixture (0.027 g) of ether, acetonitrile, and other components; (iii) a mixture (0.155 g); (iv) a mixture (0.100 g); (v) *methyl 2-(2,2,3,3,4,4,4-heptafluorobutyl)acrylate* (1) (0.081 g), b.p. 162 °C (Found: C, 35.5; H, 2.6. C₈H₇F₇O₂ requires C, 35.8; H, 2.6%); *M*⁺ 268 (required) and 237 (*M* - OMe); *v*_{max.} 3 010, 2 965, 2 855 (C-H), 1 730 (C=O), and 1 250—1 100 cm⁻¹ (C-F); φ 81.00 (3 F, t, *J* 10.5 Hz, CF₃), 114.43 (2 F, m, CF₃CF₂CF₂), and 127.78 (2 F, m, CF₃CF₂CF₂); δ 6.41 (1 H, s, olefinic H), 5.81 (1 H, s, olefinic H), 3.71 (3 H, s, MeO), and 3.17 (2 H, t, *J* 18.8 Hz, C₃F₇CH₂); and a mixture (0.023 g), not further investigated.

A portion (0.101 g) of the mixture (iii) was separated by g.l.c. (column B, 100 °C, 4 l/h N₂) to give (a) *methyl 2-methyl-2-(heptafluoropropyl)-4,4,5,5,6,6,6-heptafluorohexanoate* (2) (0.021 g); *M*⁺ 419.032 728 (*M* - F requires 419.031 654); *v*_{max.} 3 010, 2 960, 2 850 (CH), 1 756 (C=O), and 1 250—1 100 cm⁻¹ (C-F); φ 80.90 (3 F, t, *J* 10.7 Hz, CF₃CF₂CF₂), 81.48 (3 F, t, *J* 12.4 Hz, CF₃CF₂CF₂), 114.88 (2 F, m, CF₃CF₂CF₂), an AB system, δ_A 106.24, δ_B 117.32, *J*_{AB} 260 Hz (2 F, CF₃CF₂CF₂-C-CH₃), 123.06 (2 F, m, CF₃CF₂CF₂), and 128.62 (2 F, m, CF₃CF₂CF₂); δ 3.75 (3 H, s, MeO), 3.48—1.88 (2 H, m, C₃F₇CH₂), and 1.65 (3 H, s, Me). Also obtained from the mixture (iii) were fractions (b) (0.021 g) and (c) (0.012 g); fraction (c) was not identified.

Fraction (b) was shown to be *methyl 2-(heptafluoropropyl)-2-(2,2,3,3,4,4,4-heptafluorobutyl)-4,4,5,5,6,6,6-heptafluorohexanoate* (3), m.p. 33.0—33.5 °C; *M*⁺ 587.013 041 (*M* - F; C₁₄H₇F₂₀O₂ requires 587.012 643) and 575 (*M* - OMe); *v*_{max.} 3 000, 2 965 (C-H), 1 760 (C=O), and 1 250—1 120 (C-F); φ 80.98 (3 F, t, *J* 10.4 Hz, CF₃CF₂CF₂CH₂), 81.40 (3 F, t, *J* 12.3 Hz, CF₃CF₂CF₂-C-), 110.50 (2 F, m, CF₃CF₂CF₂-C-), an AB system δ_A 107.71, δ_B 116.65, *J*_{AB} 267 Hz (4 F, CF₃CF₂CF₂CH₂), 123.40 (2 F, m, CF₃CF₂CF₂-C-), and 128.66 (4 F, s, CF₃CF₂CF₂CH₂); δ 3.85 (3 H, s, OMe), and 3.64—2.45 (4 H, m, C₃F₇CH₂).

The mixture (iv) (0.100 g) was shown by ¹⁹F and ¹H n.m.r. spectroscopy to be a mixture of *methyl 2-methyl-4,4,5,5,6,6,6-heptafluorohexanoate* (4) and (*E*)-*methyl 2-methyl-4,4,5,5,6,6,6-heptafluorohex-2-enoate* (5). The i.r. spectrum showed absorption maxima at 2 990, 2 960, 2 890, 2 850 (C-H), 1 740 (C=O), 1 665 (C=C), and 1 250—1 110 (C-F); φ 81.08 [t, 9.0 Hz, CF₃CF₂CF₂ of (5)], 81.18 [t, 9.9 Hz, CF₃CF₂CF₂ of (4)], 128.25 [s, CF₃CF₂CF₂ of (5)], 128.43 [m, CF₃CF₂CF₂ of (4)], 109.89 [m, CF₃CF₂CF₂ of (5)], and 114.95 [m, CF₃CF₂CF₂ of (4)]; integration showed the ratio (4) : (5) = 3 : 1; δ 1.29 [d, *J* 7.2 Hz, Me of (4)], 2.14 [s, Me of (5)], 3.28—1.6 [m, CH₂CH< of (4)], 3.66 [s, OMe of (4)], 3.71 [s, OMe of (5)], and 6.57 [t, *J* 15 Hz, CH=CMe of (5)]. Integration of the methoxy signals showed the ratio (4) : (5) = 3 : 1. A sample of the mixture (0.5 g) was hydrogenated with a palladium on charcoal catalyst (0.03 g; 10% Pd): the product was distilled

under reduced pressure from P₂O₅ to give *methyl 2-methyl-4,4,5,5,6,6,6-heptafluorohexanoate* (4) (0.5 g), b.p. 148 °C (Found: C, 35.8; H, 3.4; F, 49.2%. C₈H₉F₇O₂ requires C, 35.6; H, 3.4; F, 49.2%); *M*⁺ 270 (required), 239 (*M* - OMe); *v*_{max.} 2 990, 2 955, 2 890, 2 850 (C-H), 1 740 (C=O), and 1 250—1 110 (C-F); φ 81.16 (3 F, t, *J* 10.0 Hz, CF₃CF₂CF₂), 115.14 (2 F, m, CF₃CF₂CF₂), and 128.62 (2 F, s, CF₃CF₂CF₂); δ 3.66 (3 H, s, OMe), 3.24—1.60 (3 H, m, CH₂CH<), and 1.30 (3 H, d, *J* 7.2 Hz, Me).

The residue from the initial distillation of the product mixture was redistilled under reduced pressure (12 mmHg) to give fraction (a) (3.34 g), b.p. 20—93 °C, fraction (b) (5.01 g), b.p. 93—122 °C, and a residue (0.15 g) which was not further investigated. A portion of fraction (a) (1.50 g) was separated by g.l.c. (column C, 130 °C, 4 l/h N₂) to afford (i) methyl 2-(heptafluoropropyl)-2-(2,2,3,3,4,4,4-heptafluorobutyl)-4,4,5,5,6,6,6-heptafluorohexanoate (3) (0.42 g), identified by i.r. spectroscopy, and (ii) a mixture (0.42 g). This was re-separated by g.l.c. (column A, 137 °C, 5 l/h N₂) to give (i) the polyfluorohexanoate (3) (0.06 g), (ii) the mixture of methyl 2-methyl-4,4,5,5,6,6,6-heptafluorohexanoate (4) and (*E*)-methyl 2-methyl-4,4,5,5,6,6,6-heptafluorohex-2-enoate (5) (0.04 g) obtained previously, and (iii) *methyl 2-(2,2,3,3,4,4,4-heptafluorobutyl)-4,4,5,5,6,6,6-heptafluorohexanoate* (6) (0.20 g), b.p. 168 °C; *M*⁺ 419.033 619 (*M* - F requires 419.031 654), 407 (*M* - OMe); *v*_{max.} 3 005, 2960 (C-H), 1 745 (C=O), and 1 250—1 120 (C-F); φ 81.30 (3 F, t, *J* 9.8 Hz, CF₃CF₂CF₂CH₂), 115.28 (2 F, br s, CF₃CF₂CF₂CH₂), and 128.61 (2 F, d, *J* 4 Hz, CF₃CF₂CF₂CH₂); δ 3.72 (3 H, s, MeO), and 3.5—2.0 [5 H, m, (C₃F₇CH₂)₂CH].

The final fraction (0.01 g) from this separation was not identified.

A portion (0.65 g) in ether of fraction (b) was separated by g.l.c. (column D, 138 °C, 6 l/h N₂) to give (i) ether; (ii) methyl 2-(heptafluoropropyl)-2-(2,2,3,3,4,4,4-heptafluorobutyl)-4,4,5,5,6,6,6-heptafluorohexanoate (3) (0.08 g), identified by i.r. spectroscopy; (iii) an inseparable mixture (0.08 g), and (±)- and meso-*dimethyl 2,3-bis(2,2,3,3,4,4,4-heptafluorobutyl)succinate* (7) (0.19 g); *M*⁺ 519.080 295 (*M* - F requires 519.084 079) and 507.061 107 (*M* - OMe requires 507.064 093); *v*_{max.} 3 000, 2 950, 2 900 (C-H), 1 730 (C=O), and 1 250—1 100 (C-F); φ (94.1 MHz) 81.06 (t, *J* 10.2 Hz, CF₃CF₂CF₂) and 81.10 (t, *J* 10.2 Hz, CF₃CF₂CF₂) (total area 3 F, the signals of *ca.* equal area), 128.60 (m, CF₃CF₂CF₂) and 128.68 (m, CF₃CF₂CF₂) (total 2 F), and broad signals at 103.18, 104.59, 106.08, 107.46, 115.86, 116.69, 118.83, and 119.57 (total 2 F). These signals were analysed as two AB systems, δ_A 104.81, δ_B 117.16, *J*_{AB} 274 Hz and δ_A 106.20, δ_B 117.96, *J*_{AB} 271 Hz; δ (100 MHz) 3.70 and 3.68 (total 3 H, both s, OMe), 3.60—1.65 (2 H, m, C₃F₇CH₂), and 1.37 and 1.28 (each 3 H, both d, *J* 3.3 Hz, Me): at 60 MHz the chemical shifts and line separation of the methyl group signals were unchanged. When the ¹H n.m.r. spectrum was taken with fluorine spin decoupling at 105 p.p.m., the two doublet signals at δ 1.37 and 1.28 ascribed to Me collapsed to singlets: irradiation at 117 p.p.m. left these signals unaffected. Decoupling the proton signals from all the fluorine signals gave a proton spectrum consisting of the two methoxy signals unchanged, two singlet lines due to Me and two AB systems of *ca.* equal intensity at δ_A 3.09, δ_B 2.02, *J*_{AB} 14.0 Hz and δ_A 2.83, δ_B 2.63, *J*_{AB} 14.0 Hz.

Two further fractions were obtained from this g.l.c. separation of fraction (b). The first of these was a liquid tentatively identified as trimethyl 1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-5,8-bis(2,2,3,3,4,4,4-heptafluorobutyl)-7-methyldodecane-5,7,8-tricarboxylate (8) (0.16 g); *M*⁺ 855.0470 (*M* - F - [CH₂=C(Me)-CO₂Me] requires 855.046 145), and 843.0180 (*M* - MeO - [CH₂=C(Me)CO₂Me]

requires 843.026 160); ν_{max} . 3 000, 2 950, 2 870 (C-H), 1 735 (C=O), and 1 300—1 100 (C-F); ϕ (94.1 MHz) 80.66—81.22 (3 F, complex, $\text{CF}_3\text{CF}_2\text{CF}_2$), 99—120 (2 F, complex, $\text{CF}_3\text{CF}_2\text{-CF}_2$), and 128.20—128.82 (2 F, complex, $\text{CF}_3\text{CF}_2\text{CF}_2$); δ (100 MHz) 3.67 (3 H, s, OMe), 3.69 (6 H, s, OMe), 2.0—3.5 (10 H, m, CH_2), and 1.49 (3 H, d, J 3.5 Hz, Me). Fluorine spin decoupling at 104 p.p.m. caused the Me signal to collapse to a singlet; decoupling of the proton resonance from all the fluorine resonances gave a series of signals at 2.0—3.5 p.p.m. consistent with overlapping AB systems.

The final compound isolated was provisionally identified as methyl 4-carboxy-6,6,7,7,8,8,8-heptafluoro-2,4-dimethyloct-2-enoate (9) (0.08 g); ν_{max} . 3 350 (OH), 3 060, 2 950, 2 870 (C-H), 1 735 (C=O), 1 650 (C=C), and 1 300—1 050 (C-F); ϕ [94.1 MHz; $(\text{CD}_3)_2\text{CO}$] 80.19 (3 F, t, J 10.0 Hz, $\text{CF}_3\text{CF}_2\text{CF}_2$), an AB system δ_{A} 114.88, δ_{B} 112.04, J_{AB} 269 Hz (2 F, $\text{CF}_3\text{CF}_2\text{-CF}_2$) and 128.01 (2 F, m, $\text{CF}_3\text{CF}_2\text{CF}_2$); δ [100 MHz, $(\text{CD}_3)_2\text{CO}$] 3.78 (3 H, s, OMe), 3.50—2.10 (2 H, m, CH_2), 1.96 (3 H, s, Me); fluorine spin decoupling reduced the complex signal at

3.50—2.10 p.p.m. to an AB system δ_{A} 3.19, δ_{B} 2.87, J_{AB} 15.6 Hz.

Acknowledgements

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