

Polyfluorobicyclo[2,2,1]heptanes. Part V.¹ Syntheses Using Bridgehead Carbanions Generated by Removal of Bridgehead Hydrogen With Aqueous Bases

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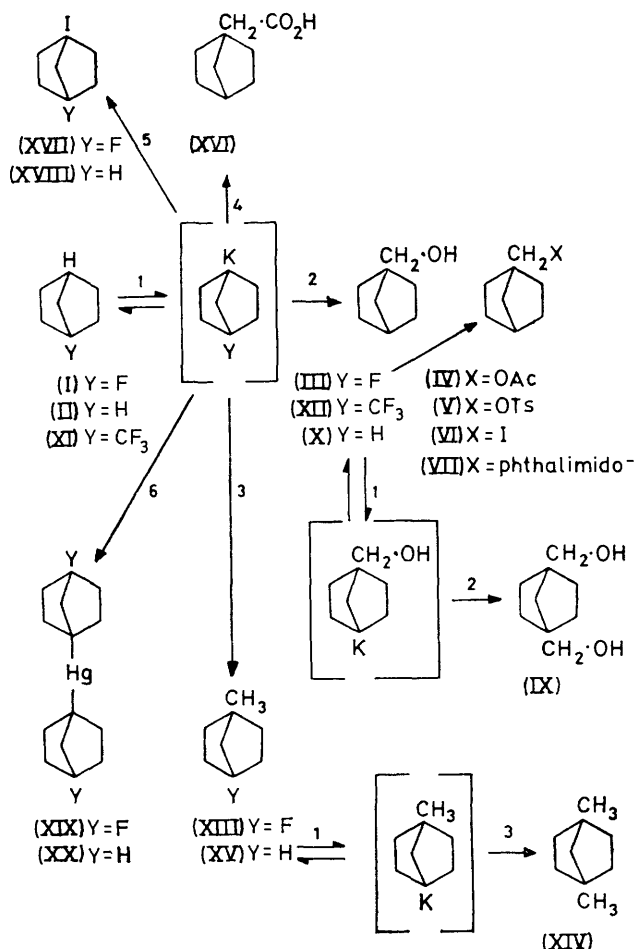
Synthetically useful carbanionic intermediates have been generated from 1*H*-undecafluoro- and from 1*H,4H*- and 1*H,4*-trifluoromethyldecafluorobicyclo[2,2,1]heptane with potassium hydroxide in water and an organic co-solvent (methanol, *t*-butyl alcohol, dimethyl sulphoxide, dimethylformamide, or dioxan). From them were prepared 1-hydroxymethyl-, 1-methyl-, and 1-iodo-undecafluorobicyclo[2,2,1]heptane, undecafluorobicyclo[2,2,1]heptan-1-ylacetic acid and bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury from 1*H*-undecafluorobicyclo[2,2,1]heptane; 1,4-bis(hydroxymethyl)-, 1*H,4*-(hydroxymethyl)-, 1*H,4*-iodo- and 1,4-dimethyl-decafluorobicyclo[2,2,1]heptane and bis-(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)mercury from 1*H,4H*-decafluorobicyclo[2,2,1]heptane; 4-trifluoromethyldecafluorobicyclo[2,2,1]hept-1-ylmethanol from 1*H*-4-trifluoromethyldecafluorobicyclo[2,2,1]heptane. The intermediate carbanions are stabilised by inductive effects alone since hyperconjugation would imply unsaturation at the bridgehead.

In hydrocarbon-type chemistry, replacement of substituents at the bridgehead positions of compounds such as bicyclo[2,2,1]heptanes is not easy. We took advantage of this² to make by direct fluorination and in good yield polyfluoro-derivatives with bridgehead hydrogen³ remaining, little fluorocarbon being formed. The reactivity of these products has been profoundly altered however because of the electronegativity of fluorine. Polyfluoro-compounds with hydrogen at the bridgehead [Scheme 1; (I), (II), and (XI)] should be convertible into carbanionic intermediates, which are favoured stereochemically, and so should be synthetically useful. It so proved: a range of bridgehead-substituted derivatives has been made¹⁻⁶ *via* bridgehead organometallic derivatives of polyfluorobicycloalkanes which were prepared using irreversible reactions with alkyl-lithium as bases under anhydrous conditions. We believe these are among the first bridgehead organometallic derivatives to be fully authenticated.⁷ Now, the generation of carbanionic intermediates from bridgehead hypopolyfluorocarbons in aqueous media has been unequivocally demonstrated, and a very convenient route to a range of polyfluorobicyclo[2,2,1]heptane derivatives has been found.

The established² stability towards elimination reactions of 1*H*-undecafluoro- (I) and 1*H,4H*-decafluoro- (II) bicyclo[2,2,1]heptane is in agreement with the absence of any ϵ dehydrofluorination path. Although the strong aqueous alkali at 100° has no effect on (I) and (II), a carbanionic intermediate is, in fact, continuously formed and reprotonated by the

water present, as shown² by deuteration if deuterium oxide is used instead of water.

The formation of such carbanionic intermediates



1, KOH-H₂O-Solvent; 2, HCHO; 3, CH₃I; 4, CH₂Br-CO₂H; 5, I₂; 6, HgCl₂-NaBr

SCHEME 1 Reactions of bridgehead hypopolyfluorobicyclo[2,2,1]heptanes in aqueous media

(All unmarked substituents are fluorine; species in brackets were not isolated)

¹ Part IV, R. Stephens, J. C. Tatlow, and K. N. Wood, *J. Fluorine Chem.*, 1971, **2**, 165.

² Part I, S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 1965, **21**, 2997.

³ Part II, S. F. Campbell, J. M. Leach, R. Stephens, and J. C. Tatlow, *J. Fluorine Chem.*, 1971, **1**, 85.

⁴ Part III, S. F. Campbell, J. M. Leach, R. Stephens, J. C. Tatlow, and K. N. Wood, *J. Fluorine Chem.*, 1971, **1**, 103.

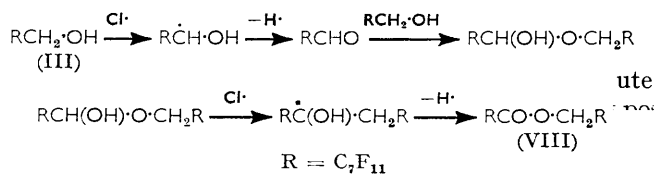
⁵ S. F. Campbell, J. M. Leach, R. Stephens, and J. C. Tatlow, *Tetrahedron Letters*, 1967, **48**, 4269.

⁶ W. B. Hollyhead, R. Stephens, J. C. Tatlow, and W. T. Westwood, *Tetrahedron*, 1969, **25**, 1777.

⁷ R. C. Fort, jun., and P. V. R. Schleyer, *Adv. Alicyclic Chem.*, 1966, **1**, 336.

has now been further substantiated in a series of synthetically useful reactions with formaldehyde, methyl iodide, iodine, bromoacetic acid, and mercuric chloride, in aqueous potassium hydroxide and an organic co-solvent. Undecafluorobicyclo[2,2,1]heptylmethanol (III) ³ (79%) was made from the 1*H*-undecafluoride (I), formalin, potassium hydroxide, and methanol. Similar observations involving 1,1,1-trifluoronitroethane ⁸ and fluorodinitromethane ⁹ have also been rationalised in terms of a carbanionic intermediate.

In the characterisation of the above alcohol (III), the acetate (IV) and tosylate (V), were prepared in the standard way and (V) was converted into the iodide (VI) and the phthalimide (VII). It was also of interest to find that the alcohol (III) and chlorine (*ca.* 2 mol.) on u.v. irradiation gave undecafluorobicyclo[2,2,1]heptylmethyl undecafluorobicyclo[2,2,1]heptyl carboxylate (VIII) as the major product (Scheme 2). The process



SCHEME 2 Photochlorination of undecafluorobicyclo[2,2,1]heptylmethanol

is presumably similar to that proposed ¹⁰ in the photochlorination of $\alpha\omega$ -trihdropolyfluoro-alcohols, and involves the intermediacy of the aldehyde hemiacetal.

A ready carbonyl addition reaction also occurred with the 1*H*,4*H*-decafluoride (II), formalin, and potassium hydroxide in either dimethyl sulphoxide (DMSO) or dimethylformamide (DMF) (but not in methanol) to give the 1,4-bis(hydroxymethyl) derivative (IX), presumably through the intermediacy of the 1*H*,4-hydroxymethyl-compound (X), since a system with two carbanionic centres in close proximity is not very likely.⁴ The mono-alcohol (X) was obtained by using a much smaller proportion of formalin.

The addition ¹ of 4-trifluoromethyldecafluorobicyclo[2,2,1]heptane (XI) to formaldehyde to give the primary alcohol (XII) (82%) was readily achieved with potassium hydroxide in methanol.

Attempts to extend the addition of the 1*H*-undecafluoride (I) to other carbonyl compounds, *e.g.* acetaldehyde, acetone, and benzaldehyde, were unsuccessful due presumably to a less favourable equilibrium constant and/or to faster competing reactions such as the aldol condensation. In this respect it was of interest to find that with formaldehyde, at high concentrations of reactants favoured a Cannizzaro reaction and consequently greatly diminished the yield of the alcohol (III). The carbanionic intermediates generated in aqueous

media were, however, shown to enter into nucleophilic substitution reactions with methyl iodide, bromoacetic acid, and iodine.

Methyl iodide and the 1*H*-undecafluoride (I) with potassium hydroxide in DMSO and water gave 1-methyl-undecafluorobicyclo[2,2,1]heptane ² (XIII) (90%). Using the same conditions the 1*H*,4*H*-decafluoride (II) gave 1,4-dimethyldecafluorobicyclo[2,2,1]heptane ⁴ (XIV) (56%) and a small amount of the 1*H*,4-methyl-decafluoride (XV).

Rapid addition of bromoacetic acid to the 1*H*-undecafluoride (I), potassium hydroxide, water, and DMSO afforded undecafluorobicyclo[2,2,1]heptan-1-ylacetic acid (XVI) (40%). Likewise, rapid addition of a suspension of iodine to the 1*H*-undecafluoride (I), potassium hydroxide, water, and methanol gave the iodide (XVII) (25%); a higher yield (73%) was obtained using the alkyl-lithium in ether.³ However, a substantial yield (64%) of the 4*H*-mono-iodide (XVIII) was obtained by the rapid addition of iodine in DMSO to the 1*H*,4*H*-decafluoride (II), potassium hydroxide, water, and DMSO [*cf.* alkyl-lithium route ⁴ (53%)]; this illustrates the synthetic advantages possible using an aqueous based system.

A recent simple, one-step synthesis of polyfluoroaryl mercurials involved mercuriation of polyfluoroarenes, such as pentafluorobenzene, under basic conditions using mercuric chloride.¹¹ The success of the method was attributed to the increased acidity of arenes resulting from fluorine substitution. In accord with these findings, the 1*H*-undecafluoride (I) and a preparation based on mercuric chloride, potassium hydroxide, water, and DMSO gave bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury (XIX) (17%), prepared (10%) previously by u.v. irradiation of the iodoundecafluoride and mercury.³ An excess of bromide ion, to minimise precipitation of mercuric oxide or basic mercuric salts,¹¹ might improve the yield of mercurial.

The addition of sodium bromide was essential in the preparation of bis-(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (XX) (10%) from the 1*H*,4*H*-decafluoride (II), mercuric chloride, potassium hydroxide, water, and DMSO. Various proportions of the same reagents without bromide gave a mixture of mercurials with molecular weights up to *ca.* 1200 and mass spectrometry indicated molecules containing two atoms of mercury.

The relatively high acidities of isolated hydrogen substituents in polyfluorides have been demonstrated both for simple systems ¹² and for bridgehead systems qualitatively ¹⁻⁶ and quantitatively.¹³ The effect is of particular importance for bridgehead systems because of the absence of concurrent elimination reactions. The bridgehead hydrogens in these polyfluoronor-

¹¹ G. B. Deacon, H. B. Albrecht, and M. J. Osborne. *Inorg. Nuclear Chem. Letters*, 1969, **5**, 985.

¹² S. Andreades, *J. Amer. Chem. Soc.*, 1964, **86**, 2003.

¹³ A. Streitwieser, jun., and D. Holtz, *J. Amer. Chem. Soc.*, 1967, **89**, 692.

⁸ E. G. German and I. L. Knunyants, *Angew. Chem. Internat. Edn.*, 1969, **8**, 349.

⁹ H. G. Adolph, *J. Org. Chem.*, 1970, **35**, 3188.

¹⁰ N. O. Bracc, *J. Org. Chem.*, 1961, **26**, 4005.

bornanes are sufficiently acidic to be replaced in aqueous media although they are activated only by simple inductive effects of fluorine. Carbanions are usually formed when unsaturated functional groups are present. Further, of course, possible resonance or hyperconjugative assistance would involve participation by contributors with unsaturation at the bridgehead—unlikely in these systems. These polyfluoronornbornanes are the first systems in which such a relatively high degree of acidity is associated with a rigidly saturated structure.

EXPERIMENTAL

Gas Chromatography.—Analytical work was carried out using a glass column 2 m long \times 4 mm diam. packed with silicone gum–Celite (1 : 5) and a nitrogen flow rate of ca. 3 l/h (Col. A) and a Pye series 104 chromatograph containing a column 4.6 m long \times 6 mm diam. packed with silicone gum–Celite (1 : 7) (Col. B) and a column 9.2 m \times 6 mm diam. packed with silicone gum–Celite (1 : 7) (Col. C). Columns B and C were also used semi-preparatively by injecting 100 μ l amounts and making appropriate adjustments to the sensitivity of the detection system.

N.m.r. Spectroscopy.—The proton spectra were measured with a Varian instrument operating at 100 MHz and the figures quoted are chemical shifts from tetramethylsilane as internal reference. ^{19}F Spectra were measured on the same instrument operating at 94.07 MHz using trichlorofluoromethane as internal reference.

Mass Spectra.—These were measured on an A.E.I. MS9 instrument.

Undecafluorobicyclo[2,2,1]heptylmethanol.—1*H*-Undecafluorobicyclo[2,2,1]heptane (20.0 g), methanol (600 ml), 40% w/v aqueous formaldehyde solution (120 ml), and KOH pellets (4.0 g) were refluxed for 2½ h. 4*N*-HCl (20 ml) was then added, and the mixture was distilled to remove volatile material and most of the methanol (ca. 500 ml); no hydrofluorocarbon was detected in the distillate by i.r. spectroscopy. The residual liquid was cooled, and water (ca. 800 ml) was added. After being kept near 0° for some time, a white crystalline precipitate was collected, washed with a little water, dried (P_2O_5) *in vacuo* for 2 days, and sublimed (100–110°, 14 mmHg) to give undecafluorobicyclo[2,2,1]heptylmethanol³ (17.4 g), m.p. 161° (sealed tube) with a correct i.r. spectrum.

The 1*H*-undecafluoride (2.0 g), *t*-butyl alcohol (100 ml), 40% formalin (20 ml), and KOH pellets (5.8 g) in the same way afforded the alcohol (1.54 g) with a correct i.r. spectrum.

Likewise, the 1*H*-undecafluoride (1.0 g), 1,4-dioxan (50 ml), 40% formalin (10 ml), and KOH pellets (0.95 g) afforded the alcohol (0.15 g); and the 1*H*-undecafluoride (2.0 g), DMSO (100 ml), 40% formalin (20 ml), and KOH pellets (1.93 g) gave the alcohol (1.6 g); both with correct i.r. spectra.

The alcohol (1.4 g), glacial acetic acid (12 ml), and concentrated H_2SO_4 (10 drops) were refluxed for 4 h, cooled, poured into water (40 ml), and extracted with ether (3 \times 10 ml) to afford, in the usual way, a liquid residue (1.5 g) which was separated by g.l.c. (Col. B; 140°) to give undecafluorobicyclo[2,2,1]heptylmethyl acetate (0.7 g), b.p. 166–168° (from P_2O_5) (Found: C, 33.2; H, 1.7; F, 56.7. $\text{C}_{10}\text{H}_5\text{F}_{11}\text{O}_2$ requires C, 32.8; H, 1.4; F, 57.1%), *m/e* 366

($\text{C}_{10}\text{H}_5\text{F}_{11}\text{O}_2$), 347 ($\text{C}_{10}\text{H}_5\text{F}_{10}\text{O}_2$), 307 ($\text{C}_7\text{F}_{11}\text{CH}_2$), 43 (overload) (CH_3CO), ν_{max} . 1765 ($>\text{C}=\text{O}$) and 2910 and 2970 cm^{-1} ($>\text{CH}$); its ^1H n.m.r. spectrum consisted of singlets at τ 7.9 (CH_3) and 5.3 ($>\text{CH}_2$).

The alcohol (8.0 g) and tosyl chloride (18.4 g) in pyridine (40 ml) afforded, following the standard procedure, the *toluene-p-sulphonate* (8.9 g), m.p. 91.5–92.5° (Found: C, 37.5; H, 1.9; S, 6.8. $\text{C}_{15}\text{H}_9\text{F}_{11}\text{O}_3\text{S}$ requires C, 37.7; H, 1.9; S, 6.7%), *m/e* 478 ($\text{C}_{15}\text{H}_9\text{F}_{11}\text{O}_3\text{S}$), 459 ($\text{C}_{15}\text{H}_9\text{F}_{10}\text{O}_3\text{S}$), 155 (base) ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$), 91 ($\text{CH}_3\text{C}_6\text{H}_4$), and 76 (C_6H_4); ν_{max} . 1600 cm^{-1} (aromatic ring).

The alcohol (5.0 g), red phosphorus (0.1 g), and iodine (2.3 g) kept in a hard-glass Carius tube (1 in \times 12 in) at 190° for 22 h afforded a crude product (5.6 g) which was shown by g.l.c. (Col. C; 150°) to contain three major and three minor components. Preparative scale g.l.c. (Col. C; 150°) gave 1-methylundecafluorobicyclo[2,2,1]heptane (ca. 0.1 g) and undecafluorobicyclo[2,2,1]heptylmethanol (trace amount) with correct i.r. spectra and undecafluorobicyclo[2,2,1]heptylmethyl iodide (0.5 g) as a colourless liquid (Found: C, 22.2; H, 0.3; I, 29.2. $\text{C}_8\text{H}_2\text{F}_{11}\text{I}$ requires C, 22.1; H, 0.4; I, 29.3%), *m/e* 415 ($\text{C}_8\text{H}_2\text{F}_{10}\text{I}$), 396 ($\text{C}_8\text{H}_2\text{F}_9\text{I}$), and 377 ($\text{C}_8\text{H}_2\text{F}_8\text{I}$); its ^1H n.m.r. spectrum consisted of a singlet at τ 6.6.

The tosylate (0.5 g) and sodium iodide (0.55 g) in DMF (5 ml) were stirred together for 3½ h at 150° to afford the iodide (0.3 g) with a correct i.r. spectrum.

The tosylate (1.98 g) and potassium phthalimide (0.83 g) in DMF were stirred for 3 h at 150° and were then poured into water (100 ml) and extracted with ether. The combined extracts gave, in the usual way, a crystalline solid (1.5 g), a portion of which was recrystallised from benzene to give *N*-(undecafluorobicyclo[2,2,1]heptylmethyl)phthalimide, m.p. 131–132° (Found: C, 42.1; H, 1.6; N, 3.0. $\text{C}_{16}\text{H}_6\text{F}_{11}\text{NO}_2$ requires C, 42.4; H, 1.3; N, 3.1%), *m/e* 453 ($\text{C}_{16}\text{H}_6\text{F}_{11}\text{NO}_2$), 434 ($\text{C}_{16}\text{H}_6\text{F}_{10}\text{NO}_2$), 160 (base) ($\text{C}_6\text{H}_5\text{NO}_2$), 104 ($\text{C}_6\text{H}_4\text{CO}$), 76 (C_6H_4), and 28 (CO), ν_{max} . 1730 ($>\text{C}=\text{O}$) and 1612 cm^{-1} (aromatic ring); its ^1H n.m.r. spectrum consisted of a singlet at τ 5.6 ($>\text{CH}_2$), and a complex multiplet at τ 2.0 (aromatic).

The alcohol (2.0 g) and chlorine (0.9 g) were irradiated with u.v. light for 89 h in a Carius tube; the pale green liquid product (1.8 g) was shown by g.l.c. (Col. A; 100°; Col. C; 120°) to contain one major and two minor components. Semi-preparative scale g.l.c. separation (Col. C; 120°) gave undecafluorobicyclo[2,2,1]heptylmethyl undecafluorobicyclo[2,2,1]heptanecarboxylate (0.4 g) as a colourless liquid (Found: C, 30.0; H, 0.4; F, 64.7. $\text{C}_{16}\text{H}_2\text{F}_{22}\text{O}_2$ requires C, 29.8; H, 0.3; F, 64.9%), *m/e* 321 ($\text{C}_7\text{F}_{11}\text{CO}$); ν_{max} . 1785 cm^{-1} ($>\text{C}=\text{O}$); its ^1H n.m.r. spectrum consisted of a singlet at τ 5.0.

1,4-Bis(hydroxymethyl)decafluorobicyclo[2,2,1]heptane.—Potassium hydroxide (2.07 g) was added to a stirred mixture of 1*H*,4*H*-decafluorobicyclo[2,2,1]heptane* (2.00 g), 37–41% (w/v) formalin (20 ml), and DMSO (100 ml) at room temperature. The mixture was stirred at room temperature for 1 h and then at ca. 75° for a further 5 h. The cold mixture was acidified with conc. HCl, poured into water (300 ml), and extracted with ether. The combined ether extracts gave, in the usual way, a residue (2.12 g), of which a part (2.00 g) was sublimed (0.01 mmHg) to give a crystalline sublimate (1.81 g) of which part (1.00 g) was crystallised twice from CCl_4 to give 1,4-bis(hydroxymethyl)decafluorobicyclo[2,2,1]heptane (0.81 g), m.p. 210–210.5° (sealed tube) (Found: C, 32.4; H, 1.8. $\text{C}_9\text{H}_6\text{F}_{10}\text{O}_2$

* This compound is highly toxic by inhalation.

requires C, 32.2; H, 1.8%), ν_{\max} 3300 cm^{-1} (OH); m/e 336 ($\text{C}_8\text{H}_6\text{F}_{10}\text{O}_2$).

Potassium hydroxide (2.17 g) was added to a stirred solution of 1*H*,4*H*-decafluorobicyclo[2,2,1]heptane (2.00 g) and 37—41% (w/v) formalin (20 ml) in DMF (100 ml) at room temperature and the mixture stirred for 1 h and then for 5 h at ca. 78°. The mixture was treated as before to give 1,4-bis(hydroxymethyl)decafluorobicyclo[2,2,1]heptane (2.08 g) with a correct i.r. spectrum.

1*H*,4-(Hydroxymethyl)decafluorobicyclo[2,2,1]heptane.—Formalin [37—41% (w/v); 0.56 ml] in water (4.5 ml) was added dropwise during 15 min to a stirred mixture of 1*H*,4*H*-decafluorobicyclo[2,2,1]heptane (2.00 g), KOH (1.91 g), DMSO (100 ml), and water (15 ml) at 75°. The mixture was stirred for a further 9½ h at 72—75° and treated as described previously, to give a liquid residue (1.89 g) which crystallised; a part (1.77 g) was sublimed (15 mmHg) to give a white solid (1.09 g). Part (1.00 g) of the latter was crystallised from CCl_4 to give white crystals (0.53 g), m.p. 176—177.5° (sealed tube), part (0.50 g) of which gave 1*H*,4-(hydroxymethyl)decafluorobicyclo[2,2,1]heptane (0.36 g), m.p. 176—177.5° (sealed tube) (from CHCl_3) (Found: C, 31.2; H, 1.4. $\text{C}_8\text{H}_6\text{F}_{10}\text{O}$ requires C, 31.4; H, 1.3%), ν_{\max} 3300 cm^{-1} (OH); m/e 306 ($\text{C}_8\text{H}_4\text{F}_{10}\text{O}$).

4-Trifluoromethyldecafluorobicyclo[2,2,1]heptan-1-ylmethanol (with K. N. Wood).—To a well-stirred solution of 1*H*-4-trifluoromethyldecafluorobicyclo[2,2,1]heptane¹ (2.0 g) and KOH (0.7 g) in MeOH (100 ml), 37—41% (w/v) formalin (20 ml) was added and the solution was refluxed for 2½ h. Addition of 4*N*-HCl (5 ml) was followed by fractional distillation of the solution to remove most of the methanol and formaldehyde. The residue was added to water (250 ml) and the precipitate was filtered off, dried, and sublimed (14 mmHg) at 100° to give 4-trifluoromethyldecafluorobicyclo[2,2,1]hept-1-ylmethanol (1.8 g), m.p. 96—97° (Found: C, 28.9; H, 0.8. $\text{C}_8\text{H}_3\text{F}_{13}\text{O}$ requires C, 28.9; H, 0.8%), ν_{\max} 3290 cm^{-1} (OH); m/e 374 (w) ($\text{C}_8\text{H}_3\text{F}_{13}\text{O}$), 30 (CH_2O); its ¹H n.m.r. spectrum consisted of singlets at τ 4.8 (OH) and 5.6 ($>\text{CH}_2$).

1-Methylundecafluorobicyclo[2,2,1]heptane.—Methyl iodide was added quickly to a stirred mixture of 1*H*-undecafluorobicyclo[2,2,1]heptane (2.00 g), KOH (1.87 g), DMSO (100 ml), and water (20 ml) at room temperature. The mixture was stirred for ½ h and then, with continued stirring, warmed to 40° during ½ h and kept at 40° for a further 2 h. KOH (4.62 g) was added and the stirred mixture was warmed to 70° during a further 2 h. Water (300 ml) was added and the mixture was boiled to give a white solid which was distilled (from P_2O_5) *in vacuo* (0.1 mmHg) to give 1-methylundecafluorobicyclo[2,2,1]heptane² (1.90 g) with a correct i.r. spectrum.

1,4-Dimethyldecafluorobicyclo[2,2,1]heptane.—Methyl iodide (8.0 ml) was added quickly to a stirred mixture of 1*H*,4*H*-decafluorobicyclo[2,2,1]heptane (2.00 g), KOH (2.31 g), DMSO (100 ml), and water (20 ml) at room temperature. The mixture was stirred for ½ h and warmed to 45°; after 2½ h, KOH (10.0 g) was added and the stirred solution was warmed to 70° during 3 h. Water (300 ml) was then added and the mixture was refluxed to give a white solid which was sublimed twice from P_2O_5 (0.1 mmHg) to give 1,4-dimethyldecafluorobicyclo[2,2,1]heptane with small quantities of 1*H*,4-methyldecafluorobicyclo[2,2,1]heptane and 1*H*,4*H*-decafluorobicyclo[2,2,1]heptane (1.73 g) as shown by g.l.c. (Col. B; 73°). Part (0.25 g) of the latter

solid in ether was separated by g.l.c. (Col. B; 52°) to give 1,4-dimethyldecafluorobicyclo[2,2,1]heptane⁴ (0.18 g) with a correct i.r. spectrum.

Undecafluorobicyclo[2,2,1]heptan-1-ylacetic Acid.—Bromoacetic acid (2.38 g) was added quickly to a stirred mixture of 1*H*-undecafluorobicyclo[2,2,1]heptane (1.00 g) and KOH (2.26 g) in DMSO (50 ml) and water (10 ml) at room temperature. The mixture was stirred for a further 1 h and then DMSO (50 ml) and water (10 ml) were added and the mixture was stirred for a further 1½ h at room temperature. Stirring was continued and the mixture was warmed to 85° during 1½ h and then kept at 85° for a further 4½ h. KOH (2.0 g) was added and the mixture was poured into water (250 ml) and extracted with ether (2 × 50 ml). The aqueous part was then acidified with conc. HCl and extracted with ether (3 × 50 ml). The combined ether extracts gave, in the usual way, a residue (0.93 g) which was sublimed to give crystals (0.48 g), m.p. 110—112° of which a portion (0.21 g) was recrystallised from CCl_4 to give undecafluorobicyclo[2,2,1]heptan-1-ylacetic acid (0.18 g), m.p. 111—112° (Found: C, 31.0; H, 0.9. $\text{C}_8\text{H}_3\text{F}_{11}\text{O}_2$ requires C, 30.7; H, 0.9%).

1-Iodoundecafluorobicyclo[2,2,1]heptane.—A suspension of resublimed I_2 (26.08 g) in MeOH (100 ml) was added during 2½ h to a refluxing solution of 1*H*-undecafluorobicyclo[2,2,1]heptane (2.00 g) and KOH (5.62 g) in MeOH (100 ml) and water (20 ml). The mixture was refluxed for a further 2½ h and then KOH (13 g) was added slowly to the boiling solution. The mixture was cooled and poured into water (950 ml) to give 1-iodoundecafluorobicyclo[2,2,1]heptane³ (0.70 g) contaminated by water and 1*H*-undecafluorobicyclo[2,2,1]heptane as shown by i.r. spectroscopy.

1*H*,4-Iododecafluorobicyclo[2,2,1]heptane.—Potassium hydroxide (1.89 g) was added to a solution of 1*H*,4*H*-decafluorobicyclo[2,2,1]heptane (2.00 g) in DMSO (90 ml) and water (20 ml). When the KOH had dissolved, the mixture was stirred at 75° for ca. ½ h and a solution of I_2 (8.31 g) in DMSO (10 ml) was quickly added. The mixture was stirred for 6½ h at 80° and 5*N*-KOH was added until the iodine colour disappeared. The cooled mixture was poured into water (300 ml), extracted with ether (3 × 50 ml) to afford, in the usual way, a yellow liquid (1.85 g) which was decanted from a white solid (0.46 g). Part (0.24 g) of the liquid was separated in 3 portions (0.08 g) by g.l.c. (Col. B; 175°) to give 1*H*,4-iododecafluorobicyclo[2,2,1]heptane⁴ (0.08 g) with a correct i.r. spectrum.

Bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury.—Mercury chloride (1.84 g) was added to KOH (1.93 g) in DMSO (100 ml) and water (20 ml) and the mixture was stirred at room temperature until (113 h) most of the precipitate had dissolved. 1*H*-Undecafluorobicyclo[2,2,1]heptane (2.00 g) was added and the mixture was stirred at room temperature for a further 73 h and was then poured into water (250 ml), made acid with conc. HCl, and extracted with ether (200 ml). The ether extract gave, in the usual way, a crystalline solid (1.55 g), a part (1.00 g) of which was crystallised from CCl_4 ; the crystalline material (0.81 g), m.p. 162—163.5° (sealed tube) sublimed to give a solid (0.70 g), m.p. 162—163.5° (sealed tube). Part (0.50 g) of the latter was recrystallised from CCl_4 to give bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury³ (0.42 g), m.p. 164.5—165.5° (sealed tube) (Found: C, 21.8; H, 0.3. Calc. for $\text{C}_{14}\text{F}_{22}\text{Hg}$: C, 21.4%); m/e ca. 765 ($\text{C}_{14}\text{F}_{21}^{198}\text{Hg}$).

Bis(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (with

F. HARDWICK).—Mercury chloride (2.7 g) was added to a stirred solution of sodium bromide (24 g) in water (40 ml); potassium hydroxide (1.1 g) was then added and the system was stirred until homogeneous. DMSO (60 ml) was then added until a precipitate began to appear when 1*H*,4*H*-decafluorobicyclo[2,2,1]heptane (5.6 g) was added. The mixture was stirred for 3 h and then poured into water (200 ml) and extracted with ether (1 × 100 ml, 2 × 50 ml). The combined ether extracts gave, in the usual way, a

solid (2.2 g) which was recrystallised from CCl₄ to give *bis*-(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (1.6 g), m.p. 214—218° (Found: C, 22.6; H, 0.3; F, 50.3. C₁₄H₂F₂₀Hg requires C, 22.4; H, 0.3; F, 50.7%); *m/e* 747 (± 5) (C₁₄H₂F₂₀Hg requires 751), ν_{\max} 3330 cm⁻¹ (\geq CH).

The authors thank Imperial Smelting Corporation Ltd. for a research grant (to J. R. T.).

[1/2011 Received, 28th October, 1971]
