Tetrahedron, 1965. Vol. 21, pp. 2997 to 3008. Pergamon Press Ltd. Printed in Northern Ireland

POLYFLUOROBICYCLO(2.2.1)HEPTANES—I

1H-UNDECAFLUORO- AND 1H,4H-DECAFLUOROBICYCLO(2.2.1)HEPTANE AND A NOVEL ELIMINATION PROCESS

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(*Received* 12 *April* 1965)

Abstract—The vapour-phase fluorination of bicyclo(2.2.1)heptadiene with cobaltic fluoride gave a complex mixture containing substantial amounts of perfluoro-, 1H-undecafluoro- and 1H,4H-decafluorobicyclo(2.2.1)heptane. The formation of perfluorocarbanions from the latter two compounds has been demonstrated by isotopic exchange in aqueous potassium hydroxide. The undecafluorobicyclo(2.2.1)heptyl anion has been formed also using methyl–lithium in ether at −55°, and trapped by reaction with acetaldehyde, bromine, methyl bromide and deuterium oxide. Near room temperature lithium undecafluorobicyclo(2.2.1)heptyl decomposed in a novel elimination process, thought to involve a transient bridgehead olefin, to give lithium fluoride and either 1-iodo-, or 1-bromo-, nonafluorobicyclo(2.2.1)hept-2-ene, depending on whether the methyl–lithium used to generate the anion was prepared from methyl iodide or methyl bromide, respectively. A similar decomposition in the presence of furan produced a furan adduct.

The partial fluorination of several hydrocarbons have been studied in this Department[1] and the techniques used have now been extended to bicyclo(2.2.1)heptadiene (I). When passed over cobaltic fluoride at 250–300° it gave a complex mixture which was separated by a combination of fractional distillation and preparative scale gas chromatography.

The most volatile components were presumed to be fragmentation products and were not examined. The second and third fractions contained perfluoromethylcyclohexane and perfluorobicyclo(2.2.1)heptane (IV). The former fluorocarbon must arise from breakage of the bridge in the bicycloheptane system, a process facilitated by the release of the strain present in the structure. Indeed, it might have been expected that little of the bicyclic ring would survive this highly exothermic process (the very volatile fragments could arise from alternative breakdown pathways and are probably based on cyclopentane and cyclohexane systems). The bicyclic fluorocarbon (IV) was surprisingly high melting (in earlier literature[2] a liquid was described, which must have been very impure) and very volatile; it was characterized by elemental analysis, mass spectrometry[3] and its formation from 1H-undecafluorobicyclo(2.2.1)heptane (III) with cobaltic fluoride.

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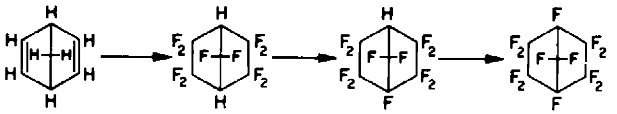
[1] M. Stacey and J. C. Tatlow in *Advances in Fluorine Chemistry* (Edited by M. Stacey, J. C. Tatlow and A. G. Sharpe) p. 176. Butterworths, London (1960); E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 159 (1959); R. J. Heitzman, C. R. Patrick, R. Stephens and J. C. Tatlow, *Ibid.* 281 (1963); J. Burdon, T. M. Hodgins, R. Stephens and J. C. Tatlow, *Ibid.* 2382 (1965).

[2] E. T. McBee and L. D. Bechtol, U.S.P. 2, 459, 781.

[3] J. R. Majer, unpublished work.



I II III IV

Fractions 4, 5, 6 and 9 from the distillation were not examined in detail, attention was confined to fractions 7, 8 and 10. Fractions 7 and 8 gave a volatile, crystalline solid, m.p. 94°, shown by elemental analysis and mass spectrometry[3] to have the formula C_7HF_{11}. The IR spectrum revealed a $\geqslant$C—H stretching frequency at the unusually high value of 3030 cm^{-1} consistent with a bridgehead position. The proton NMR spectrum consisted of a broad singlet at 3·16 ppm as expected for 1H-undecafluorobicyclo(2.2.1)heptane (III). This was confirmed by fluorination with cobaltic fluoride to give perfluorobicyclo(2.2.1)heptane (IV). The recovery of unchanged monohydro-compound (III) from this fluorination at 320° is clearly in keeping with the anticipated high chemical stability of the bridgehead hydrogen.

Fraction 10 was separated in a similar way to give a volatile crystalline solid, m.p. 92°, shown by elemental analysis to have the formula $C_7H_2F_{10}$. Again, the IR spectrum revealed a $\geqslant$C—H stretching frequency at 3032 cm^{-1}, and the proton NMR spectrum consisted of a weakly coupled band at 3·0 ppm consistent with bridgehead positions, as expected for 1H,4H-decafluorobicyclo(2.2.1)heptane (II). Mass spectrometry[3] did not give a parent molecule ion, but the fragmentation pattern was consistent with this structure, as was fluorination at 320° to 1H-undecafluoro- (III) and perfluorobicyclo(2.2.1)heptane (IV). Fraction II was pure 1H,4H-decafluorobicyclo(2.2.1)-heptane (II), the only pure component obtained from the distillation, and its substantial total yield again reflects the high chemical stability associated with a bridgehead hydrogen.

In our previous work[1] on cyclic fluorohydrocarbons, most of which have had hydrogen on secondary carbon atoms, reactions with bases have given elimination to olefins, and no evidence for the formation of fluorocarbanions could be found by deuterium exchange.

The transient formation of perfluorocarbanions from acyclic monohydrofluorocarbons bearing hydrogen in primary, secondary and tertiary positions has been demonstrated[4] by isotopic exchange in sodium methoxide–methanol solution. The relative reactivities established were rationalized in terms of hyper-conjugative (no-bond resonance) involving β-fluorine atoms; purely inductive effects were considered to play a minor role. It was of great interest, therefore, to find that both 1H-undecafluoro- (III), and 1H,4H-decafluoro- (II), bicyclo(2.2.1)heptane, whilst being recovered after treatment with strong aqueous potassium hydroxide at 100°, underwent extensive deuteration (even though in a heterogeneous system, cf. CF_3CF_2H, $CF_3CF_2CF_2H$ and CHF_3),[5] when treated with potassium hydroxide in deuterium oxide. The 1H-compound (III) gave about 80% of the deuterio-compound (V), as assessed by proton NMR spectroscopy and mass spectrometry, and this was converted back to the 1H-compound (III) by aqueous potassium hydroxide. Clearly, these exchanges show the transient formation of the carbanion (VI). In the same way the 1H,4H-compound (II) gave about 57% of the di-deuterio-compound and about 38%

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[4] S. Andreades, *J. Amer. Chem. Soc.* **86**, 2003 (1964).

[5] L. H. Slaugh and E. Bergman, *J. Org. Chem.* **26**, 3158 (1961).

of the mono-deuterio-compound; this mixture was converted back to the 1H,4H-compound (II) by aqueous potassium hydroxide. These exchanges show that bridgehead carbanions can form under the purely inductive influence of three $>CF_2$ groups in a saturated system, i.e. without resonance stabilization of the anion by neighbouring unsaturated groups (cf. bicyclo(2.2.2)octanedione-2,6),[6] as might occur in the bicyclic trisulphone of Doering and Levy.[7] It would be of added interest to compare the rates of these exchanges with those of the acyclic counterparts.[4]

The general validity of this method of deuteration was indicated by comparable exchanges with pentafluorobenzene (70%), 1H-nonafluorocyclohexene (65%) and 2-bromo-2-chloro-1,1,1-trifluoroethane (95%). The latter, in particular, is in general agreement with the published results of more precise work.[8]

The recovery of the 1H- (III) and 1H,4H- (II) compounds from the reactions involving strong aqueous alkali at 100° is in agreement with previous observations[9] that elimination processes leading to a bridgehead olefin will be extremely unfavourable when small bridges are involved (i.e. generally in bicyclo(x.y.z)alkanes when $x + y + z < 9$).[10] In the cases of II and III the carbanions formed will be rapidly re-protonated by the large excess of water present.

Trapping experiments that demonstrated the formation of heptafluoro-n-propyl- and heptafluoro-isopropyl-carbanions from the corresponding monohydroperfluorocarbons have been described by Andreades.[4] The main difficulty encountered was the extremely facile β-elimination of fluoride ion from the carbanion even at $-70°$, and yields were very low.

When 1H-undecafluorobicyclo(2.2.1)heptane (III) was treated with methyl–lithium in ether at $-40°$ until methane evolution ceased, and acetaldehyde then added, undecafluorobicyclo(2.2.1)heptyl methyl carbinol (VII) was obtained in 44% yield. The latter compound (VII) was fully characterized by IR and ^1H NMR spectroscopy, and lost the elements of water, when heated with phosphoric oxide, to give undecafluorobicyclo(2.2.1)heptyl ethylene (VIII); this was fully characterized by IR and ^1H NMR spectroscopy and mass spectrometry. Other successful trapping experiments were carried out that demonstrated the existence of the undecafluorobicyclo(2.2.1)-heptyl anion (VI). Thus, with deuterium oxide at $-55°$, 1-deutero-undecafluorobicyclo(2.2.1)heptane (V) was obtained in 60% yield and was characterized by IR and ^1H NMR spectroscopy and mass spectrometry. With bromine at $-55°$, 1-bromo-undecafluorobicyclo(2.2.1)heptane (IX) was obtained (68% yield). With methyl bromide at $-55°$, 1-methyl-undecafluorobicyclo(2.2.1)heptane (X) was obtained (50%).

It was of considerable interest to examine the thermal stability of the ethereal solution of lithium undecafluorobicyclo(2.2.1)heptyl (VI). With aqueous base the carbanion will be very rapidly reprotonated and thus, as observed, potential elimination processes will be prevented. However, when a solution of the lithium compound (VI)

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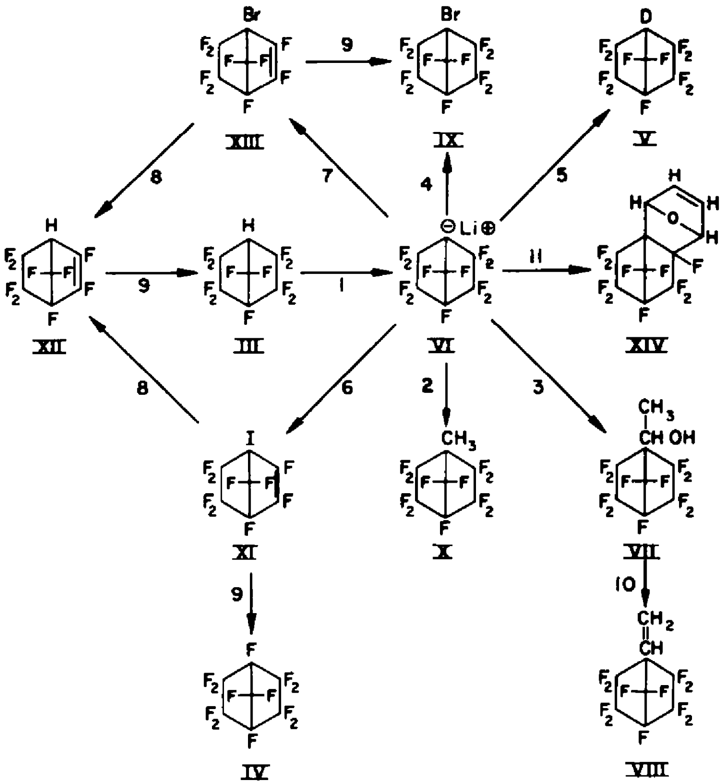
[6] P. D. Bartlett and G. F. Woods, *J. Amer. Chem. Soc.* **62**, 2933 (1940).

[7] W. V. E. Doering and L. K. Levy, *J. Amer. Chem. Soc.* **77**, 509 (1955).

[8] J. Hine, R. Wiseboeck and R. G. Ghirardelli, *J. Amer. Chem. Soc.* **83**, 1219 (1961); J. Hine, R. Wiseboeck and O. B. Ramsey, *Ibid.* **83**, 1222 (1961).

[9] E. Clar, *Ber. Dtsch. Chem. Ges.* **64**, 2200 (1931); P. D. Bartlett and L. H. Knox, *J. Amer. Chem. Soc.* **61**, 3184 (1939).

[10] Fawcett, *Chem. Rev.* **47**, 219 (1950).



Reagents: 1, MeLi (from MeBr or MeI); 2, MeBr; 3, CH_3CHO; 4, Br_2; 5, D_2O; 6, decomposition in presence of LiI; 7, decomposition in presence of LiBr; 8, (i) Mg, (ii) dil. acid; 9, CoF_3; 10, P_2O_5; 11, Furan.

in ether was allowed to attain room temperature it was noted that lithium fluoride was precipitated and, after ensuring complete decomposition by heating under reflux, an olefin was the major product (62% yield from III).

The above olefin was shown by elemental analysis and mass spectrometry to have the formula C_7F_9I. Its IR spectrum contained a strong peak at 1755 cm^{-1} characteristic of a —CF=CF— group but the frequency is higher than normally[11] observed with the flexible cyclohexene ring and may be associated with its presence in the more strained norborane system. Fluorination with cobaltic fluoride at 280° gave perfluorobicyclo(2.2.1)heptane (IV), showing that the norbornane skeleton was retained. The olefin readily gave a Grignard reagent in the usual way and this was hydrolysed to an olefin which was shown by elemental analysis and mass spectrometry to have the formula C_7HF_9. Its IR spectrum contained a strong peak at 1765 cm^{-1} characteristic of a —CF=CF— group in a norbornane system and its ^1H NMR spectrum established that a bridgehead proton was present and hence that the olefin was 1H-nonafluorobicyclo(2.2.1)hept-2-ene (XII). This structural allocation was confirmed by cobaltic fluoride fluorination, which gave 1H-undecafluorobicyclo(2.2.1)heptane (III) as the sole product (60% yield). Therefore, the iodo-olefin is 1-iodo-nonafluorobicyclo(2.2.1) hept-2-ene (XI). A minor product of the decomposition was subsequently identified as 1H-nonafluorobicyclo(2.2.1)hept-2-ene (XII) and presumably arises from the iodo-olefin (XI) *via* its lithio-compound.

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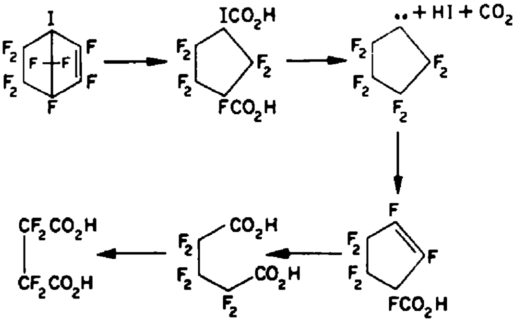
[11] J. Burdon and D. H. Whiffen, *Spectrochim. Acta* **12**, 139 (1958).

As would be expected the 1-iodo-olefin (XI) was very readily oxidized by potassium permanganate in acetone. However, tetrafluorosuccinic acid was the only acid isolated. Presumably, the intermediate heptafluoro-1-iodo-cyclopentane-1,3-dicarboxylic acid undergoes a decarboxylative α-elimination of iodide, the resultant carbene rearranges to heptafluorocyclopent-1-ene-3-carboxylic acid and this is further oxidized to tetrafluorosuccinic acid, as depicted by:



For this reason oxidation was not used in the characterization of any of the other bicyclic-olefins.

An estimation of the stability of an ethereal solution of lithium undecafluorobicyclo(2.2.1)heptyl was made by dividing the solution, kept at −55°, into three parts. The first portion was treated with acetaldehyde at −40° and gave a 40% yield of undecafluorobicyclo(2.2.1)heptyl methyl carbinol (VII). The second portion was kept at about 15° for ½ hr and then treated with acetaldehyde; this gave a 10% yield of the carbinol (VII) and an 18% yield of the iodo-olefin (XI). The third portion was refluxed for 1 hr before adding acetaldehyde, and this gave only the iodo-olefin (XI) in 40% yield. It thus appears that the decomposition is occurring quite rapidly at about 15°, but it is clearly much slower than that associated with non-bridgehead carbanions.[4,12]

This decomposition of lithium undecafluorobicyclo(2.2.1)heptyl (VI) to 1-iodononafluorobicyclo(2.2.1)hept-2-ene (XI) presumably involves an initial loss of fluoride ion in a non-coplanar β-elimination to give a transient bridgehead olefin, or diradical,[13] of very short life. This adds lithium iodide (known to be present in ethereal lithium-methyl prepared from methyl iodide). The adduct, depicted in the scheme, should then lose fluoride ion in a very facile *cis*-coplanar β-elimination[14] to give 1-iodononafluorobicyclo(2.2.1)hept-2-ene (XI). Only addition in the direction indicated can give rise to a stable product in this way.

In agreement with this scheme it was found that if the methyl–lithium, used to produce the lithium salt (VI) from the 1H-compound (III), was prepared from methyl bromide the major decomposition product was 1-bromo-nonafluorobicyclo(2.2.1)hept-2-ene (XIII). A small amount of 1-methyl undecafluorobicyclo(2.2.1)heptane (X) must arise from nucleophilic attack of the anion (VI) on excess of methyl bromide left from the methyl–lithium preparation.

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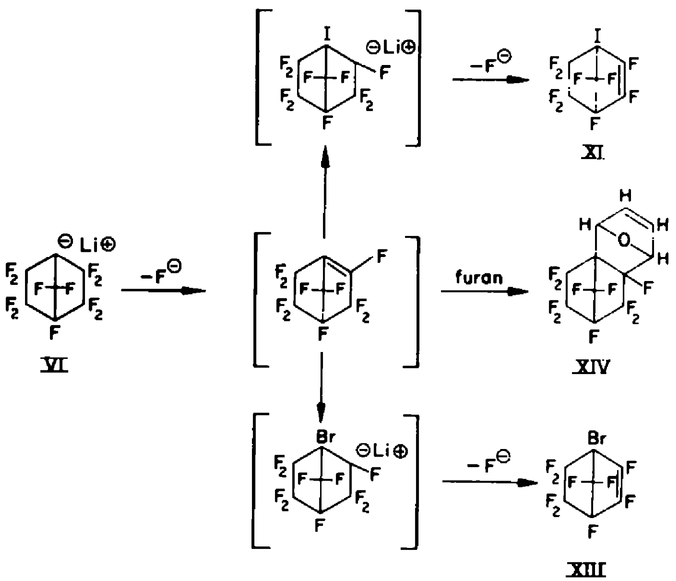
[12] D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 3036 (1964).

[13] V. Prelog, P. Barman and M. Zimmermann, *Helv. Chim. Acta* 32, 1284 (1949); W. T. Grubb and G. B. Kistiakowsky, *J. Amer. Chem. Soc.* 72, 419 (1950).

[14] N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Amer. Chem. Soc.* 85, 3199 (1963).



The 1-bromo-olefin (XIII) was shown by elemental analysis and mass spectrometry to have the molecular formula C_7BrF_9; the latter also indicated the presence of a trace of 1-bromo-undecafluorobicyclo(2.2.1)heptane (IX) which might arise from an exchange between the anion (VI) and methyl bromide. The IR spectrum of XIII contained a strong peak at 1763 cm^{-1} characteristic of a —CF=CF— group in a norbornane system. Fluorination with cobaltic fluoride at 200° gave 1-bromo-undecafluorobicyclo(2.2.1)heptane (IX) as the sole product in 90% yield (it is of interest to compare this with the fluorination of the analogous iodo-olefin (XI), in which the iodine was completely substituted). As with the iodo-olefin (XI), magnesium in ether gave from the bromo-olefin (XIII) a Grignard reagent, which was also hydrolysed to 1H-nonafluorobicyclo(2.2.1)hept-2-ene (XII).

Further evidence for the operation of the proposed mechanism was afforded by allowing the lithium compound (VI) to decompose in the presence of furan. This gave a waxy solid, shown by analytical gas chromatography to contain two roughly equal components of almost identical retention volumes, which could not be separated on a preparative scale. However, the mixture was shown by elemental analysis and mass spectrometry to have the molecular formula $C_{11}H_4F_{10}O$; a large fragment in the mass spectrum at 68 was attributed to a furan unit. The ^1H NMR spectrum clearly indicated the presence of equal numbers of vinylic and bridgehead protons (with the anticipated chemical shifts; they compared very well with those of 5,8-epoxy-1,2,3,4-tetrafluoro-5,8-dihydronaphthalene),[15] but did not permit a precise structural allocation to be made. However, the formation of two such closely similar structures (XIV) would be expected from the Diels–Alder addition of furan to a bridgehead olefin.

The above evidence strongly suggests the transient existence of unsaturation at a bridgehead position in a relatively small ring system (prior to this a bicyclo(2.2.2)octane system was the smallest considered to produce transient bridgehead unsaturation).[16]

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[15] P. L. Coe, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 3227 (1962).

[16] V. Prelog, *J. Chem. Soc.* 420 (1950).

The formation of the furan adduct (XIV), however, represents the first successful trapping of such an intermediate and further work along these lines is in progress.

EXPERIMENTAL

Gas chromatography. Analytical work was carried out using glass columns 2 m long × 4 mm diam packed with dinonyl phthalate-kieselguhr (1:2) (unit A) and a column 1 m × 4 mm packed with silicon gum-kieselguhr (1:2) (unit B). For preparative work 3 Cu-columns were used. Column A was 488 cm × 35 mm with the same packing as unit A, column B was 488 cm × 35 mm with the same packing as unit B, column C was 488 cm × 75 mm with the same packing as unit A.

NMR spectroscopy. The proton spectra were measured with a Varian instrument at 60 Mc/s, and the figures quoted are chemical shifts from tetramethylsilane as external reference.

Mass spectra[3]. These were measured on a Metropolitan-Vickers M.S.2. instrument.

Fluorination of bicyclo(2.2.1)*heptadiene*

This compound (200 g) was passed, in the usual way[1], over cobaltic fluoride (6 Kg) at 250–300° during 3 hr. The product (ca. 460 g) was completely removed from the reactor with N_2 (ca. 30 l./hr for 1½ hr), collected in a trap at −78°, washed several times with water, and then dried (P_2O_5). The total product (2·3 Kg) of five such fluorinations of bicyclo(2.2.1)heptadiene was distilled through a vacuum jacketed column (4′ × 1″) packed with Dixon gauze rings ($\frac{1}{16}$″ × $\frac{1}{16}$″). The distillation was controlled by analytical gas chromatography unit A, 100°, N_2 flow-rate 1 l./hr, and the following fractions were collected: (1) b.p. 27–66° (130 g; 6 components by GPC); (2) b.p. 66–73° (172·3 g; 2 components); (3) b.p. 73–74·9° (210 g; 2 components); (4) b.p. 74·9–75·1° (99 g; 1 component); (5) b.p. 75·1–83° (162 g; 5 components); (6) b.p. 83–86·8° (116 g; 3 components); (7) b.p. 86·8–91° (161·6 g; 4 components); (8) b.p. 91–95° (206 g; 3 components); (9) b.p. 95–109·5° (146·8 g; 5 components); (10) b.p. 109·5–112° (148·9 g; 2 components); (11) b.p. 112° (284·3 g) (1 component); (12) a residue (217 g) which was not examined.

Separation of fractions by preparative scale gas chromatography

Fraction 2 (8 g) was separated in two equal portions (column A; 70°; N_2 flow-rate 14 l./hr) to give: (i) perfluoromethylcyclohexane (4 g) with a correct IR spectrum except for a trace amount of an unidentified fluoro carbon with an identical retention volume using dinonyl phthalate and Kel-F oil as stationary phases; (ii) *perfluorobicyclo*(2.2.1)*heptane* (2·5 g) m.p. 105–107° (sealed tube). (Found: C, 26·7; H, 0·1; F, 73·0. C_7F_{12} requires: C, 26·9; H, 0; F, 73·1%); mass spectrometry gave a small top mass peak at 312 (C_7F_{12}), a large peak at 293 (C_7F_{11}—) and a consistent fragmentation pattern; this also revealed a small amount (~2%) of perfluoromethylcyclohexane.

Fraction 3 (6 g) was separated in two equal portions (column A; 70°; N_2 flow-rate 14 l./hr) to give: (i) perfluoromethylcyclohexane (4·5 g) with a fluorocarbon impurity; (ii) perfluorobicyclo-(2.2.1)heptane (0·7 g) with a correct IR spectrum.

Fraction 7 (160 g) was separated in two equal portions (column C; 92°; N_2 flow-rate 40 l./hr) to give: (i) a mixture (87 g) which was not examined; (ii) 1H-*undecafluorobicyclo*(2.2.1)*heptane* (60 g) m.p. 94–96° (sealed tube). (Found: C, 28·3; H, 0·3; F, 71·3. C_7HF_{11} requires: C, 28·6; H, 0·3; F, 71·1%); ν_{max} 3030 cm^{-1} (⩾C—H) (grating instrument); the proton NMR spectrum of a 2 M solution in hexafluorobenzene consisted of a broad singlet at 3·16; mass spectrometry[3] gave a small top mass peak at 294 (C_7HF_{11}) with fragments at 275 ($C_7HF_{10}^+$) and 225 ($C_6HF_8^+$). Fraction 8 (200 g) a solid, was dissolved in benzene and separated in six equal portions (column C, 82°, N_2 flow-rate 44 l./hr) to give: (i) a mixture (29 g) which was not examined; (ii) 1H-undecafluorobicyclo-(2.2.1)heptane (130 g) with a correct IR spectrum; (iii) benzene.

Fraction 10 (140 g), a solid, in diethyl ether was separated in two equal portions (column C; 100°; N_2 flow-rate 52 l./hr) to give: (i) ether and other minor components (45 g); (ii) 1H,4H-*decafluorobicyclo*(2.2.1)*heptane* (95 g) m.p. 92–93° (sealed tube) b.p. 112°. (Found: C, 30·6; H, 0·7; F, 68·6. $C_7H_2F_{10}$ requires: C, 30·4; H, 0·7; F, 68·8%); ν_{max} 3032 cm^{-1} (⩾C—H) (measured using a grating); the proton NMR spectrum of a 2 M solution in hexafluorobenzene had a band at 3·0 showing very weak coupling; mass spectrometry[3] did not give a peak due to the molecule ion at 276 but fragments at 257 ($C_7H_2F_9^+$), 176 ($C_5H_2F_6^+$) and 157 ($C_5H_2F_5^+$) were consistent with the structure given.

Fraction 11 was distilled from P_2O_5 to give 1H,4H-decafluorobicyclo(2.2.1)heptane (280 g) b.p. 112°, with a correct IR spectrum.

Fluorination of 1H-*undecafluorobicyclo*(2.2.1)*heptane*

This compound (2·0 g) was slowly sublimed into a steam of N_2 (3·5 l./hr) passing over stirred cobaltic fluoride at 320°. When the addition was complete the reactor was purged with N_2 (3·5 l./hr) for 2 hr, the solid product (1·7 g) collected at −180° and analytical gas chromatography of a solution in hexafluorobenzene revealed two other components which were separated (column A; 90°; N_2 flow-rate 17 l./hr) to give (i) perfluorobicyclo(2.2.1)heptane (0·6 g); (ii) 1H-undecafluorobicyclo (2.2.1)heptane (0·2 g) both had correct IR spectra.

Fluorination of 1H,4H-*decafluorobicyclo*(2.2.1)*heptane*

This compound (2·0 g) was fluorinated in the manner described previously to yield a solid (1·6 g) which was separated by preparative gas chromatography (column A, 90°, N_2 flow-rate 15 l./hr) to give: (i) perfluorobicyclo(2.2.1)heptane (0·3 g); (ii) 1H-undecafluorobicyclo(2.2.1)heptane (0·4 g); both had correct IR spectra.

Treatment of 1H-*undecafluorobicyclo*(2.2.1)*heptane with aqueous alkali*

1H-Undecafluorobicyclo(2.2.1)heptane (2·2 g) and 18 N KOH (10 ml) were shaken together in a sealed "pyrex" tube at 100° for 8 hr. The tube was then opened, the product washed with water and distilled *in vacuo* to give 1H-undecafluorobicyclo(2.2.1)heptane (2·0 g) with correct IR and proton NMR spectra (analytical gas chromatography of a solution in benzene showed only starting material).

Treatment of 1H,4H-*decafluorobicyclo*(2.2.1)*heptane with aqueous alkali*

1H,4H-Decafluorobicyclo(2.2.1)heptane (2·2 g) treated in the manner previously described gave unchanged starting material (2·1 g) with correct IR and proton NMR spectra.

Partial deuteration of 1H-*undecafluorobicyclo*(2.2.1)*heptane*

This compound (2 g), KOH (10 g) and D_2O (10 g) were shaken together in a sealed "Pyrex" tube at 100° for 3 hr. The tube was then opened and the lower layer distilled *in vacuo* to give a solid (1·8 g) with an IR spectrum different to that of the starting material; the proton NMR spectrum of a 1 M solution in hexafluorobenzene gave a weak band at the same position as that given by a 1 M solution of the starting material in hexafluorobenzene (the relative intensities indicated that about 80% deuteration had occurred). Mass spectrometry[8] gave a top mass doublet at 276, 275 ($C_7F_{10}D^+$, $C_7HF_{10}^+$) and breakdown fragments at 176, 175 ($C_5F_6D^+$, $C_5HF_6^+$) and 226, 225 ($C_6F_8D^+$, $C_6HF_8^+$), and a comparison of peak heights indicated 80% deuteration.

When this deuterated material (0·4 g) KOH (10 g) and water (10 ml) were shaken together in a sealed "Pyrex" tube at 100° for 3 hr, 1H-undecafluorobicyclo(2.2.1)heptane (0·4 g), with a correct IR spectrum, was obtained.

Partial deuteration of 1H,4H-*decafluorobicyclo*(2.2.1)*heptane*

This compound (3·0 g) was treated exactly as in the previous experiment to give a solid (2·7 g). Similarly the proton NMR spectrum of a 1 M solution in hexafluorobenzene indicated that approx 70% deuteration had occurred; mass spectrometry[8] gave a top mass triplet at 259, 258, 257 ($C_7F_9D_2^+$, $C_7HF_9D^+$, $C_7H_2F_9^+$) and breakdown fragments at 209, 208, 207 ($C_6F_7D_2^+$, C_6HFD^+, $C_6H_2F_7^+$), 178, 177, 176 ($C_5F_6D_2^+$, $C_5HF_6D^+$, $C_5H_2F_6^+$), 159, 158, 157 ($C_5F_5D_2^+$, $C_5HF_5D^+$, $C_5H_2F_5^+$), a comparison of peak heights indicated 1D,4D-decafluorobicyclo(2.2.1)heptane (ca. 57%) 1H,4D-decafluorobicyclo(2.2.1)heptane (ca. 38%) and 1H,4H-decafluorobicyclo(2.2.1)heptane (ca. 5%).

When this deuterated mixture (1·8 g) was treated with alkali as before it gave 1H,4H-decafluorobicyclo(2.2.1)heptane (1·5 g) with correct IR and proton NMR spectra.

Other partial deuterations

(a) *Pentafluorobenzene.* When this compound (3·0 g) was treated in the usual way it gave a liquid product (2·6 g) with a proton NMR spectrum that indicated approx 70% deuteration.

(b) 1H-*Nonafluorocyclohexene.* In the same way, this olefin (2·8 g) gave a liquid product (1·8 g) which proton NMR spectroscopy and mass spectrometry[8] indicated to contain approx 60% of the deuterated olefin.

(c) 1,1,1-*Trifluorochlorobromoethane.* This compound (2·0 g), KOH (1 g) and D_2O (10 g) were treated at 80–85° under a water condenser backed with a condenser at −78°, for 2 hr. The flask was then cooled and the product (1·4 g) separated and shown by analytical gas chromatography to contain one component. Proton NMR spectroscopy indicated that approx 95% deuteration had occurred.

Preparation of methyl-lithium

(a) *Methyl iodide* (54 g) in diethyl ether (150 ml) was added dropwise to a well stirred suspension of small pieces Li (5·6 g) in ether (150 ml) at −10°. After the addition was completed the mixture was stirred at −10° for 1 hr and filtered by decantation through glass wool. The solution was stored at 0° and the clear solution used after a titrimetric assay.

(b) *Methyl bromide* was bubbled through diethyl ether (300 ml) containing Li wire (4·0 g) at room temp until all the Li had reacted. The solution was filtered and stored as before.

Undecafluorobicyclo(2.2.1)heptyl methyl carbinol

To a well stirred solution of 1H-undecafluorobicyclo(2.2.1)heptane (6·0 g) in diethyl ether (80 ml) at 40°, an ethereal solution of methyl-lithium (0·98 N, from methyl iodide) was added dropwise until the evolution of methane (ca. 420 ml, at room temp and atm. press.). Stirring was continued at −40° for ½ hr, redistilled acetaldehyde (20 ml) was then added and the stirring continued for ½ hr, at −40° and for 1 hr, at room temp during which time a sticky precipitate formed. Dil. HCl (4 N, 25 ml) was then added, the ether layer separated, washed with water, dried ($MgSO_4$), filtered and most of the ether removed to leave a residue (10·5 g) shown by analytical gas chromatography (unit B; 130°, N_2 flow-rate 3 l./hr) to contain ether and one other component which was separated (column B; 110°, N_2 flow-rate 18 l./hr) to give: (i) ether (2·5 g) (ii) *undecafluorobicyclo(2.2.1)heptyl methyl carbinol* (3·0 g) m.p. 99–100°. (Found: C, 31·6; H, 1·4. $C_9H_5F_{11}O$ requires: C, 32·0; H, 1·5%); ν_{max} 3500 cm^{-1} (—O—H); the proton NMR spectrum consisted of a doublet (J = 7 c/s; CH_3), a doublet (J = 8 c/s; O—H) and a pentuplet (J = 7 c/s; C—H) in the intensity ratio 3:1:1 centred at 1·3, 1·9 and 4·3, respectively.

The carbinol (0·5 g) and a trace of hydroquinol was distilled from P_2O_5 to give *undecafluorobicyclo(2.2.1)heptyl ethylene* (0·3 g) m.p. 49–50° (sealed tube). (Found: C, 33·7; H, 1·1. $C_9H_3F_{11}$ requires: C, 33·8: H, 0·9%); ν_{max} 1648 cm^{-1} (—CH=CH_2); the ^1H NMR spectrum consisted of a group of signals centred at 5·5 (vinylic protons); mass spectrometry[8] gave a top mass peak at 320 ($C_9H_3F_{11}$) and a consistent fragmentation pattern with a large peak at 27 (−CH=CH_2).

1-*Iodononafluorobicyclo(2.2.1)hept-2-ene*

To a well stirred solution of 1H-undecafluorobicyclo(2.2.1)heptane (6·0 g) in diethyl ether (400 ml) at −55°, methyl-lithium in diethyl ether (1·1 N; prepared from MeI) was added dropwise until evolution of methane (ca. 400 ml) ceased. After addition the solution was stirred at −55° for a further ½ hr, then kept at 25–30° for ½ hr, without stirring and finally the solution was stirred under gentle reflux for 1 hr. The solution was then cooled, filtered and the solid, which had formed during the reaction, examined, it showed no definite IR spectrum, imparted a carmine colour to a Bunsen flame, and gave a positive fluoride test. The filtrate was distilled through a vacuum jacketed column (1′) packed with glass helices (the distillate was examined at regular intervals by gas chromatography and throughout only ether was detected) and the residue (50 ml) washed with water, dried ($MgSO_4$), filtered and most of the remaining ether removed by distillation through a vacuum jacketed column (6″) packed with glass helices and the residue (8·2 g) separated by gas chromatography (column B; 100°; N_2 flow-rate 17 l./hr) to give: (i) a mixture (2·4 g) shown by analytical gas chromatography (unit A, 100°, N_2 flow-rate 1 l./hr) to contain largely diethyl ether and two other minor components [further separation by gas chromatography (column A, 100°, N_2 flow-rate 17 l./hr) gave 1H-*nonafluorobicyclo(2.2.1)hept-2-ene* with a correct IR spectrum (see later)]; (ii) 1-*iodononafluorobicyclo(2.2.1)hept-2-ene* (4·8 g) b.p. 124–125°. (Found: C, 22·7; H, 0·1; I, 33·4. C_7F_9I requires: C, 22·0; H, 0; I, 33·2%); ν_{max} 1755 cm^{-1} (—CF=CF—) λ_{max} 2560 Å (ε, 520; in EtOH) mass spectrometry[8] gave a top mass peak at 382 (C_7F_9I).

This olefin (0·5 g) and $KMnO_4$ in acetone, in the usual way, evolved heat and gave tetrafluorosuccinic acid isolated as its di-anilinium salt (0·25 g) m.p. 210–211° (lit. 224°) with a correct IR spectrum.

Fluorination of 1-*iodononafluorobicyclo*(2.2.1)*hept*-2-*ene*

This compound (1·0 g) in a stream of N_2 (3·5 l./hr) was fluorinated in the usual manner over cobaltic fluoride at 280°. The crude product (0·9 g) was washed with water and distilled *in vacuo* from P_2O_5 to give *perfluorobicyclo*(2.2.1)*heptane* (0·5 g) with a correct IR spectrum. Analytical gas chromatography of a solution of the solid product both in hexafluorobenzene and perfluoromethylcyclohexane indicated only one component other than the solvent.

1H-*Nonafluorobicyclo*(2.2.1)*hept*-2-*ene*

1-Iodononafluorobicyclo(2.2.1)hept-2-ene (3·0 g) in ether (15 ml) was added to a well stirred suspension of Mg (10 g) (and a small crystal of I_2) in dry gently refluxing ether (90 ml). When reaction commenced the source of the heat was removed and the rest of the iodo-olefin added dropwise. After the addition was completed, stirring was continued at room temp for 15 min and then under reflux for 2 hr. At the end of this time dil. H_2SO_4 (3 N; 30 ml) was slowly added, the ethereal layer separated, washed with water, dried ($MgSO_4$), filtered and most of the ether removed by distillation through a vacuum jacketed column (6″) packed with glass helices. The residue (5·2 g) was separated by gas chromatography (column A; 90°; N_2 flow-rate 17 l./hr) to give: (i) ether (3 g); (ii) 1H-*nonafluorobicyclo*(2.2.1)*hept*-2-*ene* (1·4 g) m.p. 36–37°. (Found: C, 32·4 (water added to facilitate combustion); F, 66·7. C_7HF_9 requires: C, 32·8; F, 66·8%); ν_{max} 1765 cm^{-1} (—CF=CF—); the proton NMR spectrum of a 2 M solution in hexafluorobenzene consisted of a singlet at 3·3 (bridgehead proton); mass spectrometry[3] gave a top mass peak at 256 (C_7HF_9).

Fluorination of 1H-*nonafluorobicyclo*(2.2.1)*hept*-2-*ene*

This compound (0·9 g) was fluorinated over cobaltic fluoride at 140° in the usual way. The crude solid product (0·9 g) was washed with water and distilled *in vacuo* from P_2O_5 to give 1H-undecafluorobicyclo(2.2.1)heptane (0·6 g) with a correct IR spectrum.

An estimation of the stability of an ethereal solution of lithium undecafluorobicyclo(2.2.1)*heptyl*

A solution of 1H-undecafluorobicyclo(2.2.1)heptane (3·0 g) in ether (200 ml) was treated with methyl-lithium (from MeI) at −40° in the usual way, and the solution divided into 3 parts.

(A) To one portion (60 ml) at −40°, acetaldehyde (7·0 g) was added and, in the manner described previously, afforded a residue (3·7 g) which was separated by gas chromatography (column B; 100°; N_2 flow-rate 15 l./hr) to give: (i) ether (1·3 g) containing two trace components which could not be isolated; (ii) undecafluorobicyclo(2.2.1)heptyl methyl carbinol (0·4 g) with a correct IR spectrum.

(B) A second portion (60 ml) was kept at room temp for ½ hr and then acetaldehyde (7·0 g) was added, and in the usual way gave: (i) ether; (ii) 1-iodononafluorobicyclo(2.2.1)hept-2-ene (0·2 g); (iii) undecafluorobicyclo(2.2.1)heptyl methyl carbinol (0·1 g); both had correct IR spectra.

(C) A third portion (80 ml) was kept at room temp for ½ hr and then heated under reflux for 1 hr and, in the manner described previously, filtered, evaporated and the residue separated by gas chromatography to give: (i) ether; (ii) 1-iodononafluorobicyclo(2.2.1)hept-2-ene (0·6 g) with a correct IR spectrum.

1-D-*Undecafluorobicyclo*(2.2.1)*heptane*

1H-Undecafluorobicyclo(2.2.1)heptane (1·0 g) was treated with methyl-lithium (from MeBr) in ether (30 ml) at −55° in the usual way and D_2O (10·0 g) was added and the system stirred at room temp for 1 hr. The ether layer was then separated, dried ($MgSO_4$), filtered and most of the ether removed by distillation through a vacuum jacketed column (6″) packed with glass helices to leave a residue (3·3 g) which was separated by gas chromatography (column A, 85°, N_2 flow-rate 17 l./hr) to give: (i) ether (2·2 g); (ii) 1-D-*undecafluorobicyclo*(2.2.1)*heptane* (0·6 g); a 2 M solution in hexafluorobenzene gave no proton NMR signal; mass spectrometry[3] gave a top mass peak at 295 ($C_7F_{11}D$); no starting material was detected; the IR spectrum was substantially different, from 3000–650 cm^{-1}, to that of the starting material.

Decomposition of lithium undecafluorobicyclo(2.2.1)*heptyl in the presence of lithium bromide*

To a well stirred solution of 1H-undecafluorobicyclo(2.2.1)heptane (6·0 g) in ether (400 ml) at −55°, methyl-lithium in ether (1·03 N; prepared from MeBr) was added until no more methane was evolved. Treatment of the mixture as described previously gave a residue (6·3 g) which was shown by analytical gas chromatography to contain 3 major components. A portion (3·5 g) was separated on a preparative scale (column B; 70° N_2 flow-rate 16 l./hr) to give: (i) ether (0·8 g); (ii) a mixture (0·5 g) containing 1-*methylundecafluorobicyclo*(2.2.1)*heptane* (90%) (see later) and suspected 1-methylnonafluorobicyclo(2.2.1)hept-2-ene (10%)[17]; (iii) 1-*bromononafluorobicyclo*(2.2.1)*hept-2-ene* (1·3 g) b.p. 100°. (Found: C, 25·0; H, 0·1; Br, 24·3. C_7BrF_9 requires: C, 25·1; H, 0; Br, 23·9%); ν_{max} 1763 cm^{-1} (—CF=CF—); mass spectrometry[8] gave a doublet top mass peak at 336, 334 (C_7BrF_9) and indicated the presence of a small amount of 1-bromoundecafluorobicyclo(2.2.1)heptane (see later).

The above brom-olefin (1·0 g) in ether (5 ml) was added dropwise to a well stirred suspension of Mg turnings (0·3 g) in gently refluxing ether (30 ml) and, after a further 1¾ hr, dil H_2SO_4 (4 N; 25 ml) was added and the mixture stirred until two clear layers were formed. The ethereal layer was washed with water, dried ($MgSO_4$), filtered and distilled through a vacuum jacketed column (6″) packed with glass helices, and the residue (1·9 g) separated by GPC (column A; 65°; N_2 flow-rate 15 l./hr) to give: (i) ether (1·4 g) (ii) 1H-*nonafluorobicyclo*(2.2.1)*hept-2-ene* (0·5 g) with correct IR and proton NMR spectra.

1-*Bromoundecafluorobicyclo*(2.2.1)*heptane*

(a) 1-Bromononafluorobicyclo(2.2.1)hept-2-ene (0·4 g) was fluorinated in the usual way over cobaltic fluoride at 200° (N_2 flow-rate 5 l./hr) to give 1-*bromoundecafluorobicyclo*(2.2.1)*heptane* (0·4 g) with a correct IR spectrum (see later).

(b) To a well stirred solution of 1H-undecafluorobicyclo(2.2.1)heptane (2·0 g) in ether (50 ml) at −55°, methyl–lithium (1·0 N; prepared from MeBr) was added dropwise until methane (170 ml) evolution ceased. The solution was stirred at −55° for ½ hr, then Br_2 (6 g; A.R. grade) was added and the mixture stirred at −55° for ½ hr, and at room temp for 1 hr. Then water (10 ml) and $Na_2S_2O_3$ were added, the ethereal layer separated, washed with water, dried ($MgSO_4$) filtered, most of the ether removed through a vacuum jacketed column (6″) packed with glass helices and the residue (3·4 g) separated by GPC (column B; 65°; N_2 flow-rate 17 l./hr) to give: (i) ether (1·0 g); (ii) 1-*bromoundecafluorobicyclo*(2.2.1)*heptane* (1·7 g) m.p. 109–110° (sealed tube). (Found: C, 22·8; F, 56·7. C_7BrF_{11} requires: C, 22·5; F, 56·0%); mass spectrometry[8] gave a doublet top mass peak at 374, 372 (C_7BrF_{11}) and a consistent breakdown pattern.[8] The IR spectrum was identical to that of the product of the fluorination of 1-bromononafluorobicyclo(2.2.1)hept-2-ene (earlier).

1-*Methylundecafluorobicyclo*(2.2.1)*heptane*

To a well stirred solution of 1H-undecafluorobicyclo(2.2.1)heptane (1·0 g) in ether (50 ml) at −55°, methyl–lithium (0·93 N; prepared from MeBr) was added dropwise until no more methane (90 ml) was evolved. The solution was then stirred at −55° for ½ hr, and MeBr bubbled through the stirred solution for ½ hr, at −55° and for ½ hr, at 25–30°. Finally, the solution was stirred under gentle reflux for ½ hr, cooled, washed successively with dil H_2SO_4 and water, dried ($MgSO_4$), filtered and distilled through a vacuum jacketed column (6″) packed with glass helices to remove any MeBr and ether (b.r. 31–34°). The residue (1·7 g) was separated by GPC (column B; 70°; N_2 flow-rate 15 l./hr) to give: (i) ether (1·0 g); (ii) 1-*methylundecafluorobicyclo*(2.2.1)*heptane* (0·5 g) m.p. 125·5–126·5° (sealed tube). (Found: C, 31·3; H, 1·0. $C_8H_3F_{11}$ requires: C, 31·2; H, 1·0%); the proton NMR spectrum of a 1·5 M solution in hexafluorobenzene consisted of a singlet at 1·2 (—CH_3); mass spectrometry[8] gave a small top mass peak at 308 ($C_8H_3F_{11}$) and large peaks at 289 ($C_8H_3F_{10}^+$), 127 ($C_4H_3F_4^+$) and a small one at 15 (—CH_3); the IR spectrum contained no double bond absorption; (iii) a trace component which could not be isolated but which had the same retention volume as 1-bromononafluorobicyclo(2.2.1)hept-2-ene.

Control experiment

1H-Undecafluorobicyclo(2.2.1)heptane (1·0 g) was treated with methyl–lithium (prepared from MeBr) in exactly the same way but MeBr was *not* passed into the solution. The same isolation procedure gave a residue (1·8 g) which was separated by GPC (column B; 65°; N_2 flow-rate 18 l./hr) to give: (i) ether (1·0 g); (ii) 1-methylundecafluorobicyclo(2.2.1)heptane (0·1 g); (iii) 1-bromononafluorobicyclo(2.2.1)hept-2-ene (0·5 g); both with correct IR spectra.

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[17] S. F. Campbell, R. Stephens and J. C. Tatlow, unpublished work.

Decomposition of lithium undecafluorobicyclo(2.2.1)*heptyl in the presence of Furan*

To a well stirred solution of 1H-undecafluorobicyclo(2.2.1)heptane (3·0 g) in ether (50 ml) at −55°, methyl–lithium (0·93 N; made from MeBr) was added dropwise until the evolution of methane (250 ml) ceased. The solution was stirred at −55° for ½ hr, then redistilled furan (b.p. 31·2°) (10 ml) added dropwise, the solution stirred for a further ½ hr, at −55° and then kept at 25–30° for ½ hr, without stirring (during which time a solid formed.) The system was finally stirred under gentle reflux for 1 hr, cooled, filtered (0·3 g of LiF collected) and most of the ether removed by distillation through a vacuum jacketed column (6″) packed with glass helices. The residue (3·0 g) was separated by GPC (column B; 140°; N_2 flow-rate 17 l./hr) to give: (i) ether (1·0 g) (shown to contain a small amount of starting material by analytical GPC); (ii) a waxy *furan adduct* (1·6 g) [shown by analytical GPC (unit B; 130°; N_2 flow-rate ca. 0·3 l./hr) to contain two components of approx equal peak areas] m.p. 70–90°. (Found: C, 38·3; H, 1·1. $C_{11}H_4F_{10}O$ requires: C, 38·6; H, 1·2%); mass spectrometry[3] gave a top mass peak at 343 ($C_{11}H_4F_{10}O$) and a large fragment at 68 (C_4H_4O); the proton NMR spectrum of a solution in diethyl ether (1:1 w/v) consisted of two broad singlets of equal intensity at 6·5 (—CH═) and 5·3 ($\geqslant$C—H) each partly overlapped with broad multiplets of equal intensity centred at 6·4 and 5·1 (the intensity ratio of the two sets was approx 7:5); the IR spectrum of a KBr disc (containing 3 mg in 300 mg KBr) was transparent from 1800 to 1600 cm^{-1} with strong absorption from 1300 to 1200 cm^{-1} ($\geqslant$C—F).

Acknowledgements—The authors thank Dr. J. R. Majer for the mass spectral measurements and their structural interpretation and the D.S.I.R. for a maintenance grant (to S. F.C.).