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POLYFLUOROBICYCLO(2,2,1)HEPTANES
PART III*.
DERIVATIVES FROM 1*H*,4*H*-DECAFLUOROBICYCLO(2,2,1)HEPTANE

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SUMMARY

The title compound was converted *via* its mono-lithio derivative into the 1,4-disubstituted decafluorobicyclo(2,2,1)heptanes: (1)X-C_7F_{10}-Y(4), where $X = H$ and $Y = D$, $-CH(OH)CH_3$, $-Br$, $-I$, $-CO_2H$, $-CH_3$, $-CH(OH)C_6H_5$, $-C(OCOCH_3){=}CH_2$; $X = Y = D$; $X = Y = Br$; $X = Y = I$; $X = Y = CH_3$; $X = CH_3$, $Y = CO_2H$. The lithio derivative decomposed in refluxing ether *via* a transient bridgehead diradical to give 1,4-disubstituted perfluorobicyclo(2,2,1)hept-2-enes, but related Grignard reagents did not.

INTRODUCTION

The major component from the fluorination[2] of norbornadiene is 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I)**, which is now shown to be a valuable synthetic intermediate, undergoing lithiation at the bridgehead position in the same way as the 1*H*-undecafluoro analogue[1,2].

RESULTS AND DISCUSSION

Reaction between (I) and methyl-lithium in ether at −55° produced only 1 mol. (approximately) of methane before evolution ceased, and it would thus appear that the derived 1*H*,4-lithio-decafluorobicyclo(2,2,1)heptane (II) is a much weaker acid than (I) and reacts with methyl-lithium at a very much reduced rate.

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[*] For Part II, see ref. 1.

[**] This compound should be handled with extreme care. It is volatile and quite low concentrations cause rapid anaesthesia; it is toxic to small animals.

Indeed, no unequivocal evidence has been obtained for the formation of 1,4-di-lithio-decafluorobicyclo(2,2,1)heptane in the present work. This effect is consistent with the transmission through the central molecular cavity of the dipole associated with the C–Li bond, or expressed in terms of carbanionic stabilities the 1-lithio-4*H* compound (II) is more stable than the di-lithio compound, since the latter has two negative centres in close proximity.

The deuteriation of 1*H*,4-lithio-decafluorobicyclo(2,2,1)heptane (II) with deuterium oxide at −55° gave 1*D*,4*D*- (III), 1*H*,4*D*- (IV) and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) in the ratio of 7:10:3, respectively. However, little significance can be attached to this ratio, since complex equilibria will be set up. For example, lithium deuteroxide will be formed, and it is known that deuterium oxide in the presence of base will deuteriate 1*H*,4*H*-decafluorobicyclo(2,2,1)-heptane[2].

After lithiation, as described above, the 1*H*,4*H*-decafluoride (I) has been converted by standard reactions into derivatives of decafluorobicyclo(2,2,1)-heptane as follows:

acetaldehyde → 1*H*,4-(2′-hydroxyethyl)- (V);
benzaldehyde → 1*H*,4-(α-hydroxybenzyl)- (VI);
carbon dioxide → 1-carboxy, 4*H*- (VII);
acetyl chloride → 1*H*,4-(1′-acetoxyvinyl)- (VIII);
bromine → 1*H*,4-bromo- (IX), and 1,4-dibromo- (X);
iodine → 1*H*,4-iodo- (XI), and 1,4-di-iodo- (XII);
methyl iodide → 1*H*,4-methyl- (XIII) and 1,4-dimethyl- (XIV).

4*H*-Decafluorobicyclo(2,2,1)heptane-1-carboxylic acid (VII) was characterised as its s-benzylthiuronium salt. The crystalline free acid decomposed on melting probably by decarboxylation but otherwise showed no particular instability (it is more stable than the perfluoro analogue[1]).

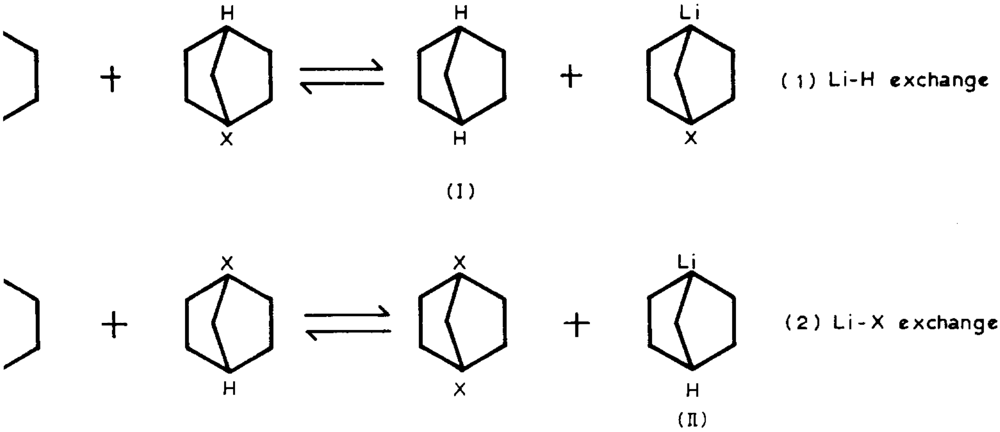
The 1*H*,4-lithio compound (II) when treated with excess acetyl chloride gave α-[4*H*-decafluorobicyclo(2,2,1)heptan-1-yl]vinyl acetate (VIII), a reaction analogous to that undergone by the 1-lithio-undecafluoro analogue[1]. In an attempt to explore this process further, methyl undecafluorobicyclo(2,2,1)heptan-1-yl ketone isolated previously[1] was treated with the 1*H*,4-lithio compound (II) in the presence of acetyl chloride. The products were (i) α-[undecafluorobicyclo-(2,2,1)heptan-1-yl]vinyl acetate, (ii) a trace of material suspected to be 1-[undecafluorobicyclo(2,2,1)heptan-1-yl)] buta-1,3-dione, (iii) a trace of α-[1*H*-decafluorobicyclo(2,2,1)heptan-4-yl]vinyl acetate (VIII) and (iv) the 1*H*,4*H*-decafluoride (I). Products (i) and (ii) arise by lithiation of the methyl ketone with (II) (giving also (I)), the tautomeric anion then reacting by *O*-acetylation to give (i) and *C*-acetylation to give (ii). Compound (VIII) arises *via* direct reaction of (II) with acetyl chloride.

Bromine and 1*H*,4-lithio-decafluorobicyclo(2,2,1)heptane (II) at −55° gave 1*H*,4-bromo- (IX), 1,4-dibromo- (X), and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane

(I) in the molar ratio of 8:32:36, respectively. Likewise, iodine gave 1*H*-4-iodo- (XI), 1,4-di-iodo- (XII), and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) in the molar ratio of 54:7:5, respectively, and methyl iodide gave 1*H*,4-methyl- (XIII), 1,4-dimethyl- (XIV), and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) in the molar ratio of 40:29:27, respectively.

Since never more than 1 mol. of methane is evolved on addition of methyllithium to the 1*H*,4*H*-fluorocarbon, the disubstituted products must arise *via* equilibria such as those depicted in Figure 1 which account for the isolation of 1*H*,4*H*-fluorocarbon in all these reactions in proportions greater than could be explained by incomplete lithiation originally.

When X = methyl in Figure 1 only proton abstraction (equilibrium (1)), is at all likely and adequately accounts for the product ratio observed, if it is assumed



(All unmarked substituents are fluorine.)

Fig. 1. Lithium exchange with the 1*H*,4-lithio-decafluoride (II).

that reaction of (II) with methyl iodide is comparable in rate with establishment of equilibrium (1) (the 1-lithio-4-methyl derivative will in turn react with methyl iodide).

When X = Br, equilibrium (1) could be rather further to the right than in the methyl series (since the electron-attracting bromine may help to stabilise the 4-bromo carbanion) and could be established rapidly relative to the rate of reaction of (II) with bromine. Further lithium–bromine exchange (equilibrium (2)) should be slow. A low yield of the 1*H*,4-bromo compound (IX) is then explicable since the 4*H* carbanion and the 4-bromo carbanion can compete for the bromine and considerable amounts of the 1,4-dibromide (X), together with (I), will be formed. In contrast, when X = I, equilibrium (1) may favour the component on the left more than when X = Br, and may also be established slowly relative to the rate of reaction of (I) with iodine. Only in this way can the products be explained, since equilibrium (2) should favour compounds (II) and (XII) if the 1*H*,4-iodide (XI) and the 1-lithio-4-iodide were ever present together in significant concentrations.

The facility of such an iodine–lithium exchange was demonstrated experimentally when 1*H*,4-iodo-decafluorobicyclo(2,2,1)heptane (XI) was heated with methyl-lithium in ether at −60°. No methane at all was evolved, but, after addition of water, 1*H*,4*H*- (I) and 1*H*,4-methyl-decafluorobicyclo(2,2,1)heptane (XIII) were formed. Lithium exchanged entirely for iodine in preference to hydrogen, (XIII) being presumably formed from the 1*H*-lithiate (II) and residual methyl iodide. It is pertinent to compare this with the analogous reaction of 1*H*,4-methyl-decafluorobicyclo(2,2,1)heptane (XIII), from which methane was evolved, and the derived lithio compound reacted with carbon dioxide to give 4-methyl-decafluorobicyclo(2,2,1)heptane-1-carboxylic acid (XV) in good yield.

A better yield (61 %) of the 1,4-di-iodide (XII) was obtained using tetrahydrofuran as solvent and 2.8 mol. of n-butyl-lithium in hexane to lithiate the 1*H*,4*H*-fluorocarbon (I). Tetrahydrofuran, by virtue of its greater cation solvating power[3], is known to be a better solvent for di-lithio derivatives[4]. However, the destabilisation resulting from such close proximity of two carbanionic centres may well still preclude the actual formation of 1,4-di-lithio-decafluorobicyclo-(2,2,1)heptane, and the formation of the di-iodide (XII) can arise *via* the equilibria depicted in Figure 1, the reactions being carried through to the di-iodide by the excess of butyl-lithium.

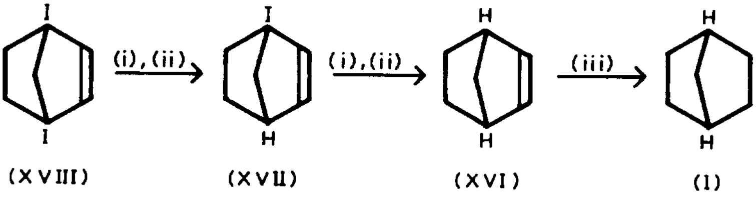
Grignard reagents were prepared from 1*H*,4-bromo- (IX), 1*H*,4-iodo- (XI) and 1,4-dibromo- (X) decafluorobicyclo(2,2,1)heptane and, in contrast to those derived from the 4-fluoro substituted bromide and iodide (see earlier[1]), were stable in refluxing ether and, after hydrolysis, gave only 1*H*, 4*H*-decafluorobicyclo(2,2,1)-heptane (I). In the case of the 1*H*,4-iodo-Grignard this stability was confirmed by the formation of 1*H*,4-(2′-hydroxyethyl)-decafluorobicyclo(2,2,1)heptane (V) with acetaldehyde.

The lower stability[1] of the 4-fluorosubstituted Grignard reagents relative to these may result from an interaction within the central molecular cavity (*cf.* ref. 5) between the dipole associated with the carbon–fluorine bond and the carbanionic centre of the carbon–magnesium bond, which in turn favours loss of fluoride ion from C_2[6].

1*H*,4-Iodo-decafluorobicyclo(2,2,1)heptane (XI) and lithium aluminium hydride (LAH) gave the 1*H*,4*H*-fluorocarbon in agreement with a positive character for the iodine similar, even if diminished with respect, to that established for the 4-fluoro substituted analogue[1].

In view of the higher thermal stabilities of the 4*H*-substituted Grignard reagents, it was of interest to examine the thermal stability of an ethereal solution of 1*H*,4-lithio-decafluorobicyclo(2,2,1)heptane (II).

With aqueous base it has been found[2] that 1*H*,4*H*-decafluorobicyclo(2,2,1)-heptane (I) does not undergo elimination, presumably giving a carbanion which is rapidly re-protonated. However, when an ethereal solution of 1*H*,4-lithio decafluorobicyclo(2,2,1)heptane (II) was allowed to attain room temperature, lithium fluoride was precipitated and after ½ h reflux, to ensure complete decomposition, a mixture of olefins was produced, *viz.*, 1*H*,4*H*-octafluorobicyclo(2,2,1)hept-2-ene (XVI), 1*H*,4-iodo-octafluorobicyclo(2,2,1)hept-2-ene (XVII) and 1,4-diiodo-octafluorobicyclo(2,2,1)hept-2-ene (XVIII) in the mol. ratio of 1:2:1, respectively (see Figure 3). They were identified by IR and NMR spectroscopy and mass spectrometry, and unequivocally related to 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) by step-wise conversion of iodine to hydrogen by forming Grignard reagents and treating each with aqueous acid, and finally saturating the double bond with fluorine as depicted in Figure 2.



(i) Mg ; (ii) 5$\underline{N}$ HCl ; (iii) CoF_3

(All unmarked substituents are fluorine.)

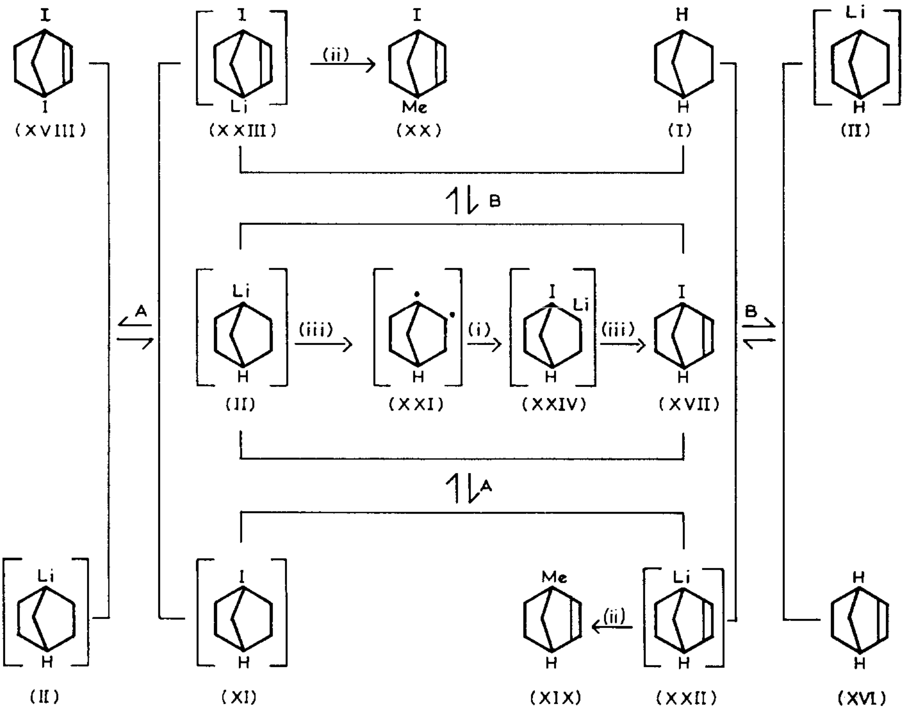
Fig. 2. Grignard characterisations.

The Grignard reagents involved in the sequence of Figure 2, like those derived from 1-bromo- and 1-iodo-nonafluorobicyclo(2,2,1)hept-2-ene[2, 6], displayed a high stability in refluxing ether.

When the decomposition of the lithio derivative (II) was repeated, and different GLC conditions were employed during the separation, besides (XVI)–(XVIII), small amounts of two additional products were isolated, *viz.*, 1*H*-4-methyl-octafluorobicyclo(2,2,1)hept-2-ene (XIX) and 1-iodo-4-methyl-octafluorobicyclo-(2,2,1)hept-2-ene (XX).

It seems reasonable to assume that the decomposition involves only the 1*H*,4-lithio compound (II) which, as depicted in Figure 3, loses lithium fluoride in a non-coplanar β-elimination to give the transient bridgehead diradical (XXI) in the same way as the known lithium undecafluorobicyclo(2,2,1)heptyl[1, 2]. Addition of lithium iodide (known to be present in ethereal methyl-lithium prepared from methyl iodide) gives (XXIV) which loses lithium fluoride to give the 1*H*-4-iodo-2-ene (XVII), the major individual product. Only addition in the direction indicated can give rise to a stable product in this way.

The other two main products ((XVI) and (XVIII)) of the decomposition can then derive from the 1*H*,4-iodo olefin (XVII) and the 1-lithio-4*H* compound (II) as indicated in Figure 3 by a complex series of equilibria. In a lithium–iodine



(i) LiI ; (ii) MeI ; (iii) loss of LiF

Equilibrium A: Li–I exchange.
Equilibrium B: Li–H exchange.

(All unmarked substituents are fluorine. Species in brackets were not isolated.)

Fig. 3. Decomposition of lithiated 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I).

exchange equilibrium, the saturated 1*H*,4-iodide- (XI) and 4*H*-octafluorobicyclo-(2,2,1)hept-2-enyl lithium (XXII) would be given, and in a lithium–hydrogen exchange equilibrium, the 1*H*,4*H*-decafluoride (I) and 4-iodo-octafluorobicyclo-(2,2,1)hept-2-enyl lithium (XXIII). The inequality of these two equilibria need not affect the outcome of the decomposition since two further equilibria can be set up involving each of the above four compounds. Thus, (XI) and (XXIII) produce the 1,4-di-iodo olefin (XVIII) and the 1*H*,4-lithio compound (II) by lithium–iodine exchange, and (I) and (XXII) produce the 1*H*,4*H* olefin (XVI) and the 1*H*,4-lithio compound (II) by proton-abstraction. Some of the unsaturated lithio derivatives, ((XXII) and (XXIII)) being more stable, may survive to give (XVI) and (XVII) by reaction with water in the work-up. The mol. ratio of the final products is consistent with these interactions.

The minor products ((XIX) and (XX)) arise from the reaction of small amounts of methyl iodide (which may not be present in all preparations), residual from the preparation of the methyl-lithium used to generate the 1*H*,4-lithio compound (II), with the thermally stable intermediate heptenyl lithiums ((XXII) and (XXIII)).

Despite its apparent lower acidity in quantitative measurements[7], the 1*H*,4*H*-decafluorobicycloheptane (I) resembles the 1*H*-undecafluoride in undergoing lithiation readily, thereby becoming a versatile synthetic intermediate. It gives rise according to the conditions to ranges of polyfluoro derivatives mono- or di-substituted at the bridgehead positions by reactions specific so far to the fluorocarbon series.

EXPERIMENTAL

Apparatus

Gas chromatography, spectroscopy *etc.* were as described[1] in Part II.

Preparative

1,4-Dideutero- (III) and 1H-4-deutero-decafluorobicyclo(2,2,1)heptane (IV)

1*H*,4*H*-Decafluorobicyclo(2,2,1)heptane (I) (2.0 g) and methyl lithium (0.9 *N*) in ether were mixed as before, D_2O (10.0 g) added and the stirred mixture allowed to attain room temperature during ¾ h. The ether layer afforded a residue (4.0 g) which was separated by GLC (col. Q; 100°; N_2, 18 l/h) to give ether and a mixture (1.9 g) which was shown to contain 1,4-dideutero-decafluorobicyclo(2,2,1)heptane (35 %), 1*H*,4-deutero-decafluorobicyclo(2,2,1)heptane (50 %) and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (15 %) by mass spectrometry (Metropolitan-Vickers MS2 instrument).

1-(4H-Decafluorobicyclo(2,2,1)heptane-1-yl)ethanol (V)

1*H*,4*H*-Decafluorobicyclo(2,2,1)heptane (3.0 g) and methyl lithium (1.16 *N*) in ether were mixed in the usual way, re-distilled acetaldehyde (10 ml) added and stirring continued at —55° for ¼ h then at room temperature for 1 h, during which time a sticky ppt. formed. 4 *N* H_2SO_4 (20 ml) was then added, and the ether layer gave, in the usual way, a residue (5.0 g) which was separated by GLC (col. B; 130°; N_2, 16 l/h) to give three fractions besides ether. Fraction (i) (1.0 g) was shown to contain a small amount of starting material by GLC (col. O; 100°; N_2, 1 l/h). Fraction (ii) was 1-(4*H*-decafluorobicyclo(2,2,1)heptan-1-yl)ethanol (V) (nc) (2.0 g), m.p. 94–95° (after sublimation, 14 mm/20°) (Found: C, 33.7; H, 1.7. $C_9H_6F_{10}O$ requires C, 33.8; H, 1.9 %); it had $\nu_{max.}$ 3400 cm^{-1} (OH), and its ^1H NMR spectrum consisted of a doublet centred at 1.33 ($J = 7$ cps) (CH_3), a singlet at 2.4 (OH), a singlet at 3.2 (bridgehead proton) and a multiplet centred at 4.4 ($J = 7$ cps) ($\geqslant$C–H) in the relative intensity ratio of 3:1:1:1, respectively (Varian 60 Mcps). Fraction (iii) was a sticky yellow oil (1.0 g) $\nu_{max.}$

ca. 3400 (OH), 2900 (CH) and 1700 cm^{-1} ($\rangle$C=O) which was not examined further.

4H-Decafluorobicyclo(2,2,1)heptan-1-yl benzyl alcohol (VI)

1*H*,4*H*-Decafluorobicyclo(2,2,1)heptane (I) (3.0 g) and methyl-lithium (1.8 *N* from MeI) in ether were mixed as before, re-distilled benzaldehyde (10 ml) added and the stirring continued for a further 1 h after warming slowly to room temperature. After the standard procedure, the ethereal layer gave a residue (9.2 g) which was separated by GLC (col. B; 170°; N_2, 15 l/h) to give ether (3.1 g) and a yellow oil which gradually solidified and was recrystallised twice from light petroleum (b.p. 40–60°) to give 4*H*-decafluorobicyclo(2,2,1)heptan-1-ylbenzyl alcohol (VI) (nc) (0.8 g) m.p. 80–81° (Found: C, 44.1; H, 2.3. $C_{14}H_8F_{10}O$ requires C, 44.0; H, 2.1 %), $\nu_{max.}$ 3455 cm^{-1} (OH) and 1493 cm^{-1} (aromatic ring).

4H-Decafluorobicyclo(2,2,1)heptane-1-carboxylic acid (VII)

The 1*H*,4*H*-decafluoride (I) (10 g) and methyl-lithium (1.5 *N* from MeBr) in ether were mixed as before, and the solution treated with carbon dioxide to give, after sublimation (14 mm) and recrystallisation from CCl_4, 4*H*-decafluorobicyclo(2,2,1)heptane-1-carboxylic acid (6.1 g) (VII) (nc) m.p. 177–178° (decomp.) (Found: C, 30.1; H, 0.5; F, 59.3. $C_8H_2F_{10}O_2$ requires C, 30.0; H, 0.6; F, 59.4%), $\nu_{max.}$ *ca.* 3000 (OH) and 1750 cm^{-1} ($\rangle$C=O), *m/e* 320 (vw) with intense fragments at 257 ($C_7H_2F_9$), 144 (C_4F_5H) and 44 (CO_2) and a base peak at 113 (C_3HF_4), its ^{1}H NMR spectrum consisted of bands at 5.7 τ and -1.9 τ in the relative intensity ratio of 1:1. The acid gave an s-benzylthiuronium salt (nc) m.p. 148–149° (decomp.) (from water) (Found: C, 40.0; H, 2.7; F, 39.2; N, 5.8; S, 6.5. $C_{16}H_{12}F_{10}N_2O_2S$ requires C, 39.5; H, 2.5; F, 39.1; N, 5.8; S, 6.6 %).

α-(4H-Decafluorobicyclo(2,2,1)heptan-1-yl)vinyl acetate (VIII)

1*H*,4*H*-Decafluorobicyclo(2,2,1)heptane (3.0 g) and methyl-lithium (1.6 *N* from MeI) in ether were mixed in the usual way and re-distilled acetyl chloride (10 ml) slowly added. The solution was stirred at $-50°$ for 30 min, and for a further 1 h after attaining room temperature, and water added. The ethereal layer, treated in the manner described previously, gave a residue (4.3 g) which was separated by GLC (col. B; 110°; N_2, 15 l/h) to give: (i) ether (1.4 g); (ii) 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (0.8 g) with a correct IR spectrum; (iii) α-(4*H*-decafluorobicyclo(2,2,1)heptan-1-yl) vinyl acetate (VIII) (nc) (0.6 g) b.p. 205–207° (Found: C, 37.0; H, 1.8. $C_{11}H_6F_{10}O_2$ requires C, 36.7; H, 1.7 %), $\nu_{max.}$ 1781 ($\rangle$C=O), and 1658 cm^{-1} ($\rangle$C=CH$_2$), *m/e* 360 ($C_{11}H_6F_{10}O_2$), its ^{1}H NMR spectrum consisted of a sharp singlet at 1.9 (CH_3), a broad singlet at 3.6 (bridgehead proton) and a multiplet centred at 5.4 (vinylic protons) in the relative intensity ratio of 3:1:2, respectively.

Reaction of methyl undecafluorobicyclo(2,2,1)heptan-1-yl ketone with 1H,4-lithio-decafluorobicyclo(2,2,1)heptane (II) and acetyl chloride

This ketone (0.3 g) in dry ether (5 ml) was added to the ethereal solution obtained from 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (0.5 g) and methyl-lithium at −60° (*ca.* 50 ml, methane evolved), acetyl chloride (1 ml) added, the mixture allowed to attain room temperature gradually and then treated as above; the residue was separated by GLC (col. E; 78°; N_2, 5 l/h) to give (a) ether and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (with correct retention volumes on col. G; 100°; N_2, 1 l/h); (b) α-(undecafluorobicyclo(2,2,1)heptan-1-yl)vinyl acetate (0.15 g) with a correct IR spectrum; (c) suspected 1-(undecafluorobicyclo(2,2,1)-heptan-1-yl) buta-1,3-dione (trace amount), $\nu_{max.}$ 1787 and 1746 cm^{-1} ($\rangle C=O$), *m/e* 378 ($C_{11}H_5F_{11}O_2$); (d) α-(4*H*-decafluorobicyclo(2,2,1)heptan-1-yl)vinyl acetate (VIII) (trace amount) with a correct retention volume.

1H,4-Bromo- (IX) and 1,4-dibromo-decafluorobicyclo(2,2,1)heptane (X)

1*H*,4*H*-Decafluorobicyclo(2,2,1)heptane (I) (3.0 g) and methyl-lithium (1.0 *N* from MeBr) in ether were mixed as before and bromine (6.0 g) added. The solution, treated as described previously, gave a residue (4.8 g) which was separated by GLC (col. B; 125°; N_2, 14 l/h) to give three fractions. Fraction (i) was a mixture (2.5 g), which on further separation by GLC (col. Q; 100°; N_2, 16 l/h) gave (a) ether and (b) 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (1.0 g) with a correct IR spectrum. Fraction (ii) was 1*H*,4-bromo-decafluorobicyclo-(2,2,1)heptane (IX) (nc) (0.3 g), m.p. 110–111° (sealed tube) (Found: C, 23.6; H, 0.0; F, 54.0. C_7HBrF_{10} requires C, 23.7; H, 0.3; F. 53.5 %), *m/e* 354–356 (C_7HBrF_{10}) and a consistent fragmentation pattern (Metropolitan-Vickers MS2); its ^1H NMR spectrum in hexafluorobenzene consisted of a broad singlet at 3.9 (Varian 60 Mcps). Fraction (iii) was 1,4-dibromo-decafluorobicyclo(2,2,1)heptane (X) (nc) (1.4 g) m.p. 94–96° (Found: C, 19.2; H, 0.0; Br, 36.2. $C_7Br_2F_{10}$ requires C, 19.4; Br, 36.9 %), mass spectrometry did not give an accurate top mass peak but breakdown fragments indicated the presence of two bromine atoms (Metropolitan-Vickers MS2).

1H-4-Iodo-decafluorobicyclo(2,2,1)heptane (XI)

1*H*,4*H*-Decafluorobicyclo(2,2,1)heptane (10.0 g) and methyl-lithium (0.7 *N* from MeBr) in ether were mixed as before, and re-sublimed iodine (30 g) in dry ether (120 ml) was added drop-wise and the solution allowed to gradually attain room temperature. Excess iodine was removed by washing with a solution of $Na_2S_2O_3$ in water, and the ethereal layer treated as usual. The combined residues (39 g) from two such experiments were separated by GLC (col. C; 140°; N_2, 58 l/h) to give three fractions besides ether (10 g). Fraction (i) was 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (1.0 g) (I) with a correct IR spectrum. Fraction (ii) was 1*H*,4-iodo-decafluorobicyclo(2,2,1)heptane (XI) (nc) (15.5 g) m.p. 102–103°

(sealed tube) (Found: C, 20.8; H, 0.0; I, 31.7. $C_7HF_{10}I$ requires C, 20.9; H, 0.2; I, 31.6 %), *m/e* 402 ($C_7HF_{10}I$) and a consistent fragmentation pattern; the ^{1}H NMR spectrum of a solution in CCl_4 consisted of a broad singlet at 3.75 ($\geqq$CH). This iodide (XI) (0.52 g) and LAH (0.2 g) in ether (10 ml) at 0° afforded 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (0.2 g) with a correct IR spectrum. Fraction (iii) was 1,4-di-iodo-decafluorobicyclo(2,2,1)heptane (XII) (nc) (2.6 g) with a correct IR spectrum (see later).

1H,4-Methyl- (XIII) and 1,4-dimethyl-decafluorobicyclo(2,2,1)heptane (XIV)

The 1*H*,4*H*-decafluoride (I) (3.0 g) and methyl-lithium (1.25 *N* from MeBr) in ether were mixed as before and methyl iodide (5 ml) was added. The mixture was allowed to attain room temperature slowly, stirred for 12 h, 4 *N* HCl (30 ml) added, and the ethereal layer separated and treated in the normal way, to leave a residue (7.6 g) which was separated by GLC (col. F; 70°; N_2; 6.5 l/h) to give: (i) ether (3.4 g); (ii) 1,4-dimethyl-decafluorobicyclo(2,2,1)heptane (XIV) (nc) (0.9 g) m.p. 128.5–129.5° (Found: C, 35.4; H, 1.8. $C_9H_6F_{10}$ requires C, 35.5; H, 2.0 %), *m/e* 304 ($C_9H_6F_{10}$), its ^{1}H NMR spectrum in CCl_4 consisted of a singlet at 1.5 (CH_3); (iii) 1*H*,4-methyl-decafluorobicyclo(2,2,1)heptane (XIII) (nc) (1.2 g) m.p. 117–118° (Found: C, 33.5; H, 1.4. $C_8H_4F_{10}$ requires C, 33.1; H, 1.4 %), *m/e* 290 ($C_8H_4F_{10}$), its ^{1}H NMR spectrum in CCl_4 consisted of singlets at 1.5 (CH_3) and 3.46 (CH) in the relative intensity ratio of 3:1, respectively; (iv) 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (0.8 g) with a correct IR spectrum.

Reaction of 1H,4-iodo-decafluorobicyclo(2,2,1)heptane (XI) with methyl-lithium

To a well-stirred solution of the title compound (1.5 g) in ether (30 ml) at —60°, an ethereal solution of methyl lithium (1.2 *N*, from MeBr) was added. No methane was evolved, and after allowing the solution to warm to —20° 4 *N* HCl (20 ml) was added. The ether layer gave, in the usual way, a residue (3.1 g) which was separated by GLC (col. A; 95°; N_2, 33 l/h) to give: (i) ether (0.9 g); (ii) 1*H*,4-methyl-decafluorobicyclo(2,2,1)heptane (XIII) (0.2 g); (iii) 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (0.4 g) (I); (ii) and (iii) had correct IR spectra.

4-Methyl-decafluorobicyclo(2,2,1)heptane-1-carboxylic acid (XV)

1*H*-4-Methyl-decafluorobicyclo(2,2,1)heptane (XIII) (13.0 g) and methyl lithium (1.5 *N* from MeBr) in ether were mixed as usual, and the mixture treated with CO_2 in the usual manner to give, after sublimation (14 mm), 4-methyl-decafluorobicyclo(2,2,1)heptane-1-carboxylic acid (XV) (nc) (12.2 g) m.p. 120–121° (decomp.) (Found: C, 32.1; H, 1.2. $C_9H_4F_{10}O_2$ requires C, 32.3; H, 1.2 %), $\nu_{max.}$ 3500 and *ca.* 3000 cm^{-1} (OH) and 1760 cm^{-1} ($>$C=O), *m/e* 334 (w) ($C_9H_4F_{10}O_2$), 158 (intense) ($C_5H_3F_5$), 44 (intense) CO_2, its ^{1}H NMR spectrum consisted of bands at 8.5 τ and —0.4 τ in the relative intensity ratio of 3:1, respectively. The acid and a saturated solution of s-benzylthiuronium chloride in water gave s-benzylthiuronium 4-methyl-decafluorobicyclo(2,2,1)heptan-1-carboxylate monohydrate (nc) m.p. 138° decomp. (from water) (Found: C, 39.3; H, 2.9; N, 5.9. $C_{17}H_{14}F_{10}N_2O_2S.H_2O$ requires C, 39.4; H, 3.1; N, 5.4 %).

1,4-Di-iodo-decafluorobicyclo(2,2,1)heptane (XII)

To a well-stirred solution of 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (3.0 g) in THF (50 ml) at −70°, a solution of butyl-lithium in hexane (12 ml; 2.6 *N*) and THF (25 ml) was added drop-wise. After stirring for 30 min, at −70°, re-sublimed iodine (10 g) in THF (100 ml) was added and the solution allowed to attain room temperature. Unreacted iodine was removed by washing with $Na_2S_2O_3$ solution, ether (100 ml) added, and most of the THF removed by repeated washing with water. The ethereal layer gave, in the usual way, a residue (12.5 g), shown by analytical GLC (col. H; 128°; N_2, 5 l/h) to contain three components which were separated (col. B; 130°; N_2, 11 l/h) to give a mixture of ether and THF and 1,4-di-iodo-decafluorobicyclo(2,2,1)heptane (XII) (nc) (3.5 g) m.p. 61–62° (sealed tube) (Found: C, 16.1; H, 0.0; I, 47.9. $C_7F_{10}I_2$ requires C, 15.9; I, 48.1 %), *m/e* 528 ($C_7F_{10}I_2$).

1H-Decafluorobicyclo(2,2,1)hept-4-yl magnesium bromide

1*H*-4-Bromo-decafluorobicyclo(2,2,1)heptane (IX) (0.7 g) in ether (5 ml) was added to magnesium turnings (0.6 g) in gently refluxing ether (30 ml) and, after a further 1½ h, 4 *N* HCl (40 ml) was added and the mixture treated in the standard manner to leave a residue (3.3 g) which was separated by GLC (col. B; 70°; N_2, 15 l/h) to give ether (2.0 g) and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (0.4 g) with a correct IR spectrum.

Decafluorobicyclo(2,2,1)heptyl-1,4-di-magnesium bromide

The dibromo compound (X) (0.5 g) in ether (10 ml) was added drop-wise to magnesium (0.6 g) (activated with MeI) in gently refluxing ether (30 ml), and after 1½ h the mixture was treated in the standard manner to leave a residue (2.3 g) which was separated by GLC (col. B; 70°; N_2, 17 l/h) to give: (i) ether (1.6 g); (ii) 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (0.2 g) with a correct IR spectrum; (iii) trace components which could not be isolated.

1H-Decafluorobicyclo(2,2,1)heptan-4-yl magnesium iodide

1*H*-4-Iodo-decafluorobicyclo(2,2,1)heptane (XI) (2.5 g) in dry ether (40 ml) was added drop-wise to magnesium turnings (1.0 g) and a crystal of iodine in gently refluxing ether (10 ml). After 4 h reflux, freshly-distilled acetaldehyde (5 ml) was added drop-wise at 0°. The copious yellow ppt. produced was separated from unreacted magnesium by repeated decantation with ether, and hydrolysed by drop-wise addition of 4 *N* HCl (20 ml). Treatment of the ethereal layer in the manner described previously left a residue (6.5 g) which was separated by GLC (col. B; 95°; N_2, 12 l/h) to give: (i) a mixture which was separated (col. A; 75°; N_2, 20 l/h) into ether (2.7 g) and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (0.4 g) with a correct IR spectrum; (ii) 1-(4*H*-decafluorobicyclo(2,2,1)heptan-1-yl)-ethanol (V) (0.8 g) with a correct IR spectrum.

1*H*,4-Iodo-decafluorobicyclo(2,2,1)heptane (XI) (0.5 g), ether (10 ml), magnesium turnings (0.2 g) and a crystal of iodine were refluxed for 4 h, and the solution decanted from the unreacted magnesium, cooled to 0° and 4 *N* HCl (10 ml) added. The ethereal layer was separated and treated in the usual way to leave a residue, which was separated by GLC (col. A; 85°; N_2, 22 l/h) to give ether (0.8 g) and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (0.25 g) with a correct IR spectrum.

Decomposition of 1H,4-lithio-decafluorobicyclo(2,2,1)heptane (II) in ether containing lithium iodide

1*H*,4*H*-Decafluorobicyclo(2,2,1)heptane (I) (6.0 g) and methyl-lithium (1.1 *N* from MeI) in ether were mixed as before (*ca.* 500 ml, methane evolved). The solution, which contained a buff coloured ppt., was stirred at −55° for 15 min, then kept at 25–30°, without stirring, for 30 min, and finally the solution was stirred under gentle reflux for 30 min. The solution was cooled, filtered (2.0 g LiF collected) and distilled through a vacuum-jacketed column (30 cm), packed with glass helices, to remove most of the ether. The residue (*ca.* 40 ml) was washed successively with water, dilute acid and water, dried ($MgSO_4$), and most of the remaining ether removed through a vacuum-jacketed column (15 cm) packed with glass helices, and the residue (8.9 g) separated by GLC (col. B; 115°; N_2 18 l/h) to give products (i)–(iii). Product (i) was a mixture (3.0 g) which was further separated (col. Q; 82°; N_2, 18 l/h) to give (a) ether, (b) 1*H*,4*H*-octafluorobicyclo-(2,2,1)hept-2-ene (XVI) (nc) (1.0 g) with a correct IR spectrum. Product (ii) was 1*H*,4-iodo-octafluorobicyclo(2,2,1)hept-2-ene (XVII) (nc) (2.9 g) m.p. 36–37°, b.p. 144–145° (Found: C, 22.8; H, 0.1; I, 34.0. C_7HF_8I requires C, 23.1; H, 0.3; I, 34.9 %) and product (iii) 1,4-di-iodo-octafluorobicyclo(2,2,1)hept-2-ene (XVIII) (nc) (2.0 g) b.p. 196-197° (Found: C, 17.1; H, 0.0; I, 51.9. $C_7F_8I_2$ requires C, 17.1; I, 51.8 %).

The decomposition was repeated and it gave, as above, a residue (9.0 g) which was separated by GLC (col. B; 115°; N_2, 17 l/h) to give products (i)–(iv).

Product (i) was a mixture (3.6 g) which was further separated (col. Q; 100°; N_2, 17 l/h) to give (a) ether; (b) a further mixture (1.0 g) [which was dissolved in ether and re-separated (col. B; 72°; N_2, 17 l/h) to give: (b) (i) ether; (b) (ii) 1*H*,4*H*-octafluorobicyclo(2,2,1)hept-2-ene (XVI) (0.6 g) with a correct IR spectrum; (b) (iii) 1*H*-4-methyl-octafluorobicyclo(2,2,1)hept-2-ene (XIX) (nc) (0.1 g), m.p. 54–56° (sealed tube) (Found: C, 37.9; H, 1.8. $C_8H_4F_8$ requires C, 38.1; H, 1.6 %)]; and (c) 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (trace amount) with a correct IR spectrum. Product (ii) was 1*H*-4-iodo-octafluorobicyclo(2,2,1)hept-2-ene (XVII) (2.5 g) with a correct IR spectrum and product (iii) suspected 1-iodo-4-methyl-octafluorobicyclo(2,2,1)hept-2-ene (XX) (0.2 g) (Found: C, 25.9; H, 0.9. $C_8H_3F_8I$ requires C, 25.4; H, 0.8 %). Product (iv) was 1,4-di-iodo-octafluorobicyclo(2,2,1)-hept-2-ene (XVIII) (1.5 g), with a correct IR spectrum.

Characterisation of 1H-4-iodo-octafluorobicyclo(2,2,1)hept-2-ene (XVIII) and the 1H,4H-ene (XVI)

The IR spectrum of (XVII) displayed an absorption at 1754 cm^{-1} (–CF=CF–). The ^1H NMR spectrum of a solution in hexafluorobenzene consisted of a broad singlet at 3.6 (Varian 60 Mcps). Mass spectrometry gave a top mass peak of 364 (C_7HF_8I) and a consistent fragmentation pattern (Metropolitan-Vickers MS2 instrument).

The iodo olefin (XVII) (3.1 g) in ether (15 ml) was added to magnesium (1.0 g) in refluxing ether (90 ml), and after 1 h the mixture was treated as described previously to give a residue (4.4 g) which was separated by GLC (col. Q; 100°; N_2, 17 l/h) to give: (i) ether (2.2 g); (ii) 1*H*,4*H*-octafluorobicyclo(2,2,1)hept-2-ene (XVI) (nc) (1.6 g) m.p. 46–47° (Found: C, 34.9; H, 1.1. $C_7H_2F_8$ requires C, 35.3; H, 0.8 %), $\nu_{max.}$ 1765 cm^{-1} (–CF=CF–), *m*/*e* 238 ($C_7H_2F_8$) and a consistent fragmentation pattern (Metropolitan-Vickers MS2). The ^1H NMR spectrum of (XVI) consisted of a singlet at 3.16 (Varian 60 Mcps). This dihydro-olefin (XVI) (1.1 g) in a stream of nitrogen (10 l/h) was fluorinated over CoF_3 at 100° in the usual manner, and the crude solid product (1.1 g) washed with water and distilled *in vacuo* (0.1 mm) from P_2O_5 to give 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (I) (1.0 g) with a correct IR spectrum.

Characterisation of 1,4-di-iodo-octafluorobicyclo(2,2,1)hept-2-ene (XVIII)

The IR spectrum displayed an absorption at 1753 cm^{-1} (–CF=CF–), *m*/*e* 494 ($C_7F_8I_2$) and a consistent fragmentation pattern (Metropolitan-Vickers MS2).

The di-iodo olefin (XVIII) (1.4 g) in ether (5 ml) was added to magnesium (1.0 g) in refluxing ether (30 ml), and after a further hour the mixture was treated as described previously to give a residue (3.0 g) which was separated by GLC (col. B; 60°; N_2, 15 l/h) to give: (i) ether; (ii) 1*H*-4-iodo-octafluorobicyclo(2,2,1)-hept-2-ene (XVII) (0.3 g); (iii) 1,4-di-iodo-octafluorobicyclo(2,2,1)hept-2-ene (XVIII) (0.8 g), both with correct IR spectra and (ii) having a correct GLC retention time (col. P; 104°; N_2, 3 l/h).

Characterisation of 1H-4-methyl-octafluorobicyclo(2,2,1)hept-2-ene (XIX)

The IR spectrum displayed an absorption at 1755 cm^{-1} (–CF=CF–), *m*/*e* 252 ($C_8H_4F_8$) and a consistent fragmentation pattern (Metropolitan-Vickers MS2); its ^1H NMR spectrum in hexafluorobenzene consisted of a broad singlet (bridgehead proton) and a singlet (–CH_3) centred at 3.1 and 1.08, respectively (Varian 60 Mcps) (integration was not possible since a signal from a small amouut of ether overlapped the broad singlet).

Characterisation of 1-iodo-4-methyl-octafluorobicyclo(2,2,1)hept-2-ene (XX)

The IR spectrum displayed absorptions at 2900 (CH) and 1746 cm^{-1} (–CF = CF–). The ^1H NMR spectrum consisted of a singlet at 1.53 (CH_3) (Varian 60 Mcps).

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