*Journal of Fluorine Chemistry*, 15 (1980) 139–161

Received: September 26, 1979

# POLYFLUOROBICYCLO[2,2,2]OCTANES. PART III. SYNTHESES AND REACTIONS OF NEW MONO- DI- AND TRIHYDRIDES AND DERIVED COMPOUNDS

J. BATTERSBY, R. STEPHENS, J.C. TATLOW AND L.F. THOMAS

Chemistry Department, The University of Birmingham,
P.O. Box 363, Birmingham B15 2TT (Great Britain).

## SUMMARY

Fluorobicyclo[2,2,2]octanes as follows were made by fluorination with cobaltic fluoride :- 1H- and 2H-tridecafluoro- ; 1H,2H- , 1H,3H- , 2H,2H- , 2H,3H- , and 1H,4H- dodecafluoro- ; 1H,2H,3H- , 1H,2H,4H- , and 1H,3H,3H- undecafluoro- ; 2H,2H,3H,3H- decafluoro- . These afforded, by the appropriate dehydrofluorinations, dodecafluoro- ; 1H- and 2H- undecafluoro- ; 1H,2H- , 1H,3H- , and 1H,4H- decafluoro- bicyclo[2,2,2]oct-2-ene. Self-consistent nmr data confirmed all structures. 1H-Trideca- and 1H,4H-dodeca- fluorobicyclo[2,2,2]octanes possess acidic bridgehead hydrogens, which are reactive under basic conditions, and may be replaced by various functional groups. 1-Lithiotridecafluorobicyclo[2,2,2]octane, a remarkably stable perfluoroalkyl lithium derivative, survived many hours in refluxing ether, but slowly decomposed to 1- substituted undecafluorobicyclo-[2,2,2]oct-2-enes, via a transient intermediate, a bridgehead 'olefin' 'violating' Bredt's rule.

## INTRODUCTION

This study began [1] because highly fluorinated bicyclo[2,2,1]-heptanes (norbornanes) have shown many interesting features [2]. The key compounds have hydrogen at a bridgehead position, which can be substituted readily, in marked contrast to the difficulty of replacement of any bridgehead groups in hydrocarbon analogues. Synthetically-valuable metallic derivatives are made by exchanges using an alkyl lithium [3,4] or potassium hydroxide [5]. From them iodides were obtained,and thence the first bridgehead Grignard reagents [3]. Noteworthy also has been our collaboration with Streitwieser and Holtz [6]; they have measured kinetic acidities on some of these compounds, the structural features present having special significance.

Of considerable interest as well were the decompositions [3,4,7] of bridgehead lithium norbornane derivatives, via transient intermediates shown to be bridgehead 'olefins' which 'violate' Bredt's rule. It is now acknowledged [8] that our paper in 1965 [7] described the first example of these; this particular fluorocarbon species significantly pre-dated the hydrocarbon analogue.

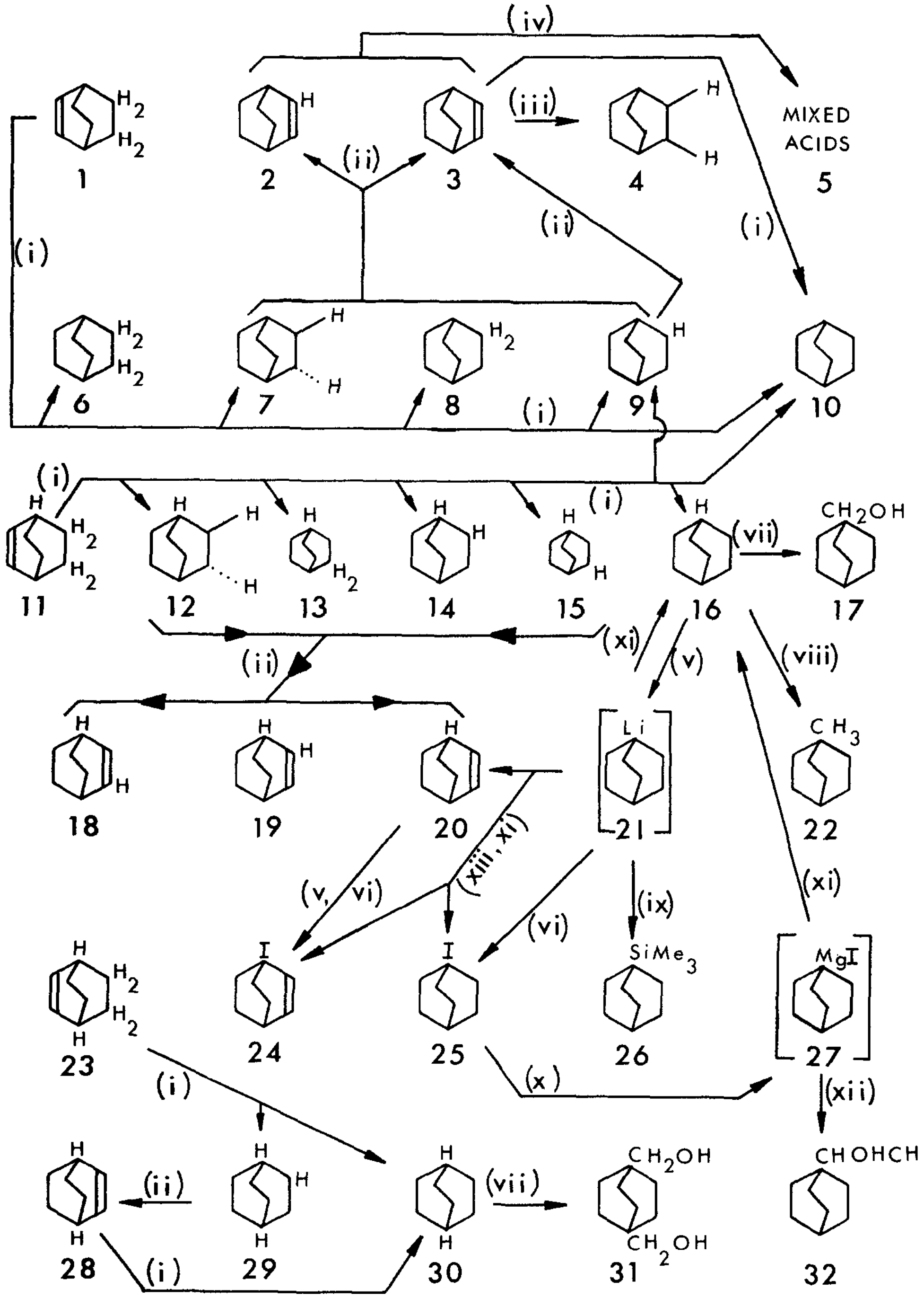
We now record investigations completed some 10 years ago on the related range of fluorobicyclo[2,2,2]octanes. The same broad features of reactivity were exhibited, showing that the fluoronorbornanes are not unique. However, significant differences were shown up in fluorobicyclo-octane chemistry, including some not readily explicable.

In our first approach [9], Diels-Alder adducts of 1H-heptafluorocyclohexa - 1,3-diene and methyl acrylate were fluorinated, the carboxylmethyl group was lost, and 1H-tridecafluoro-bicyclo[2,2,2]octane (16) synthesised. A better route was needed however, particularly so since in this series fluorination of the hydrocarbon itself with metal fluorides gives rise [10] to skeletal rearrangements. Work described here was based on Diels-Alder adducts [1] of ethylene and octafluoro- , 1H-heptafluoro- and 1H,4H-hexafluoro- cyclohexa-1,3-diene. Fluorination of these with cobalt trifluoride gave a convenient entry into the polyfluorobicyclo[2,2,2]octane series.

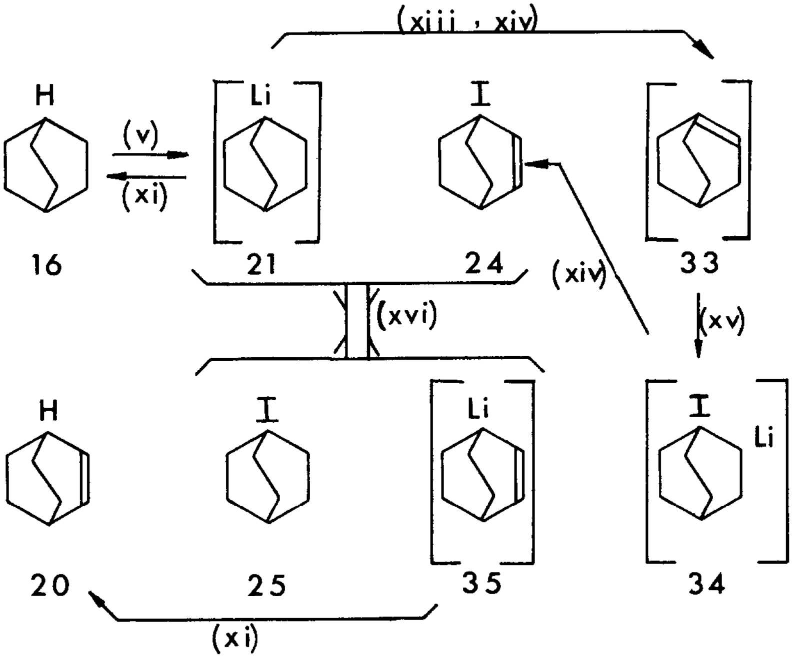
## RESULTS AND DISCUSSION

Fluorinations - The fluorinations carried out, and reactions of the products obtained, are summarised in Scheme 1. The $C_2H_4$ - $C_6F_8$ adduct [1,2,3,4,5,5,6,6-octafluorobicyclo-[2,2,2]oct-2-ene(1)]was fluorinated over cobalt trifluoride at 180° in the standard way [11] to give a mixture separable by gas chromatography, and consisting of 5 volatile but high-melting solids :- a trace of the known [9] fluorocarbon of the series (10), and 4 new polyfluorides, shown by nmr spectroscopy (Tables 1 and 2) and further reactions to be 2H-trideca- (9), 2H,2H-dodeca- (8), 2H/3H-dodeca- (7), and 2H,2H,3H,3H-deca- (6) fluorobicyclo[2,2,2]octane. Compounds 6,7 and 8 gave 9 and 10 on further reaction with cobalt trifluoride at 320°, and 9 gave 10. For adduct (1) a relatively low fluorination temperature was chosen to maximise the retention of hydrogen.

The $C_2H_4$ - $C_6HF_7$ adduct (11) was fluorinated at 280° to give four dodeca- and undeca- products (12 - 15), the 1H-tridecafluoride (16) characterised previously [9] and traces of 9 and 10. A higher fluorination temperature was used in this case, since compound 16 was required in quantity, and preliminary experiments showed that compounds 12-15 were in any case difficult to separate. Compounds actually isolated (besides 9 and 10) were 16 (mainly) and in small quantities a dodecafluoride (14) and an undecafluoride (12); two other compounds (13, 15) were obtained together in rather larger quantity, but as a mixture which could not be separated. Nmr data showed that 14 was the 1H,2H-dodecafluoride, and that 12 was the 1H,2H/3H (trans)-undecafluoride (Table 2) as would be expected for a fluorination product, where trans-arrangements of $>$ CHF.CHF $<$ are usually formed preferentially [12,16]. The nmr spectrum of the mixture (13 + 15) showed peaks entirely consistent (Table 2) with its being the 1H,3H-dodecafluoride (15) and the 1H,3H,3H-undecafluoride (13) in proportions of 7:3 respectively.



SCHEME 1 (LEGEND OPPOSITE)



SCHEME 2

ALL UNMARKED BONDS ARE TO FLUORINE.

SPECIES IN BRACKETS WERE NOT ISOLATED.

REAGENTS

(i) $CoF_3$ (ii) KOH (iii) $H_2$/Pd (iv) $KMnO_4$

(v) MeLi or BuLi (vi) $I_2$ (vii) KOH/DMSO/FORMALDEHYDE

(viii) KOH/DMSO/MeI (ix) $ClSiMe_3$ (x) Mg/$Et_2O$

(xi) $H_2O$ (xii) ACETALDEHYDE (xiii) $Et_2O$—LONG REFLUX

(xiv) LOSS OF LiF (xv) LiI (xvi) EQUILIBRIUM

Table 1.

$^{19}F$ Resonance spectra of Fluorobicyclo[2,2,2]oct-2-enes

| Compound | Ref. No. (Scheme 1) | Ring Positions 1 | 2 | 3 | 4 | 5,5' | 8,8' | 6,6' | 7,7' |
|---|---|---|---|---|---|---|---|---|---|
| perfluoro | 3 | 223.8 | 149.3 | 149.3 | 223.8 | 124.3, 126.7 | | | |
| 1H | 20 | - | 134.3 | 147.2 | 221.9 | 122.8, 125.1 | | 110.8, 113.2 | |
| 1H,4H | 28 | - | 134.0 | 134.0 | - | 110.0, 112.4 | | | |
| 2H | 2 | 211.4 | - | 116.3 | 222.2 | 123.7, 128.0 | | 122.7, 125.4 | |
| 1H,2H | 19 | - | - | 115.0 | 222.3 | 122.7, 125.9 | | 109.4, 111.8 | |
| 1H,3H | 18 | - | 99.8 | - | 210.8 | 122.6, 125.7 | | 110.2, 114.9 | |
| 5H,5'H,6H,6'F | 1 | 200.7 | 152.8 | 152.8 | 200.7 | - | 129.4* | - | 129.4* |
| 1H,5H,5'H,6H,6'H | 11 | - | 139.1 | 153.6 | 203.1 | - | 128.9 ,130.7 | - | 114.7,116.4 |
| 1H,4H,5H,5'H,6H,6'H | 23 | - | 139.2 | 139.2 | - | - | 114.3 ,118.1 | - | 114.3,118.1 |
| 2H,5H,5'H,6H,6'H | + | 185.6 | - | 120.1 | 202.1 | - | 128.2 ,131.9 | - | 127.8* |
| 1I | 24 | - | 117.3 | 147.0 | 222.0 | 120.5, 122.7 | | 104.5, 109.5 | |

*AB quartets insufficiently resolved to determine separate shifts

+ This was prepared analogously [1] to compound 11, from 2H-heptafluorocyclohexa-1,3-diene [23] (157g) in a 2 litre autoclave with ethylene (initial pressure 50 atm) for 21 h at 220°, yielding 1,2,4,5,5,6,6-heptafluorobicyclo[2,2,2]-oct-2-ene nc (157g).
(Found: C, 41.7; H, 2.1; F, 57.2. $C_8HF_7$ requires C, 41.0; H 2.1; F, 56.8%); m/e 234 (M); ir 3110 $cm^{-1}$ (=CH), 1685 $cm^{-1}$ (-CH=CF-).

Table 2.
$^{19}F$ Resonance spectra of Fluorobicyclo[2,2,2]octanes

<table>
<tr><th rowspan="2">Compound</th><th rowspan="2">Ref. No.<br>(Scheme 1)</th><th colspan="12">Ring Positions</th></tr>
<tr><th>1</th><th>2</th><th>2'</th><th>3</th><th>3'</th><th>4</th><th>5,5'</th><th>8,8'</th><th>6,6'</th><th>7,7'</th></tr>
<tr><td>perfluoro</td><td>10</td><td>221.9</td><td colspan="4">123.2</td><td>221.9</td><td colspan="4">123.2</td></tr>
<tr><td>1H</td><td>16</td><td>-</td><td colspan="2">110.7</td><td colspan="2">122.3</td><td>221.7</td><td colspan="2">122.3</td><td colspan="2">110.7</td></tr>
<tr><td>1H,4H</td><td>30</td><td>-</td><td colspan="4">109.8</td><td>-</td><td colspan="4">109.8</td></tr>
<tr><td>2H</td><td>9</td><td>213.0</td><td>-</td><td>217.3</td><td colspan="2">107.9,127.2</td><td>221.3</td><td colspan="2">122.0, 123.7 ←?→</td><td colspan="2">120.3,123.9</td></tr>
<tr><td>2H,3H/(<u>cis</u>)</td><td>4</td><td>213.2</td><td>-</td><td>224.1</td><td>-</td><td>224.1</td><td>213.2</td><td>*</td><td>*</td><td>*</td><td>*</td></tr>
<tr><td>2H/3'H (<u>tr</u>)</td><td>7</td><td>212.7</td><td>-</td><td>204.4</td><td>204.4</td><td>-</td><td>212.7</td><td>*</td><td>*</td><td>*</td><td>*</td></tr>
<tr><td>1H,2H</td><td>14</td><td>-</td><td>-</td><td>208.8</td><td>107.6</td><td>121.0</td><td>221.6</td><td>*</td><td>*</td><td>*</td><td>*</td></tr>
<tr><td>1H,3H</td><td>15</td><td>-</td><td>93.4</td><td>109.4</td><td>-</td><td>216.5</td><td>213.3</td><td colspan="2">122.8, 125.5</td><td colspan="2">111.0</td></tr>
<tr><td>1H,2H,4H</td><td>29</td><td>-</td><td>-</td><td>208.3</td><td>93.2</td><td>109.4</td><td>-</td><td>*</td><td>*</td><td>*</td><td>*</td></tr>
<tr><td>1H,2H/3'H</td><td>12</td><td>-</td><td>-</td><td>193.0</td><td>204.3</td><td>-</td><td>214.2</td><td>*</td><td>*</td><td>*</td><td>*</td></tr>
<tr><td>1H,3H,3'H</td><td>13</td><td>-</td><td colspan="2">86.8</td><td>-</td><td>-</td><td>205.5</td><td colspan="2">128.1</td><td colspan="2">111.4</td></tr>
<tr><td>2H,2'H</td><td>8</td><td>205.0</td><td>-</td><td>-</td><td colspan="2">101.2</td><td>221.3</td><td colspan="2">124.0</td><td colspan="2">127.7</td></tr>
<tr><td>2H,2'H,3H,3'H</td><td>6</td><td>201.8</td><td>-</td><td>-</td><td>-</td><td>-</td><td>201.8</td><td colspan="4">128.8</td></tr>
<tr><td>1-CH$_2$OH</td><td>17</td><td>-</td><td colspan="2">116.8</td><td colspan="2">122.7</td><td>223.4</td><td colspan="2">122.7</td><td colspan="2">116.8</td></tr>
<tr><td>1CH$_2$OH,4CH$_2$OH</td><td>31</td><td>-</td><td colspan="4">116.3</td><td>-</td><td colspan="4">116.3</td></tr>
<tr><td>1-SiMe$_3$</td><td>26</td><td>-</td><td colspan="2">108.8</td><td colspan="2">123.3</td><td>225.4</td><td colspan="2">123.3</td><td colspan="2">108.8</td></tr>
<tr><td>1-Me</td><td>22</td><td>-</td><td colspan="2">118.3</td><td colspan="2">122.2</td><td>223.0</td><td colspan="2">122.2</td><td colspan="2">118.3</td></tr>
</table>

* Complex

The $C_2H_4$ - $C_6H_2F_6$ adduct (23) was fluorinated at 225° to give traces of 10 and 16, but mainly the new 1H,2H,4H-undecafluoride (29) and 1H,4H-dodecafluoride (30) (note the nmr spectrum - Table 2). Each of these was further fluorinated at 320° to 10 and 16.

In all the fluorinations, good recoveries were obtained, and no products of skeletal rearrangement could be detected. In accordance with results in the norbornane series [7,13] the bridgehead hydrogens were replaced by fluorine much more slowly than were the others, even at higher temperatures.

Dehydrofluorinations - Again in conformity with the behaviour [7] of polyfluoronorbornanes with bridgehead hydrogen, the bicyclo-octanes 16 and 30 were unaffected by molten potassium hydroxide at 200 - 210°, in marked contrast to the ready dehydrofluorinations [14 - 17] of mono- and di- hydro-polyfluoro-cycloalkanes with 4, 5, 6, and 7- membered rings. Fluorobicyclo-octanes with hydrogen elsewhere could be dehydrofluorinated however.

The 2H- compound (9) reacted with molten potassium hydroxide to give the dodecafluoro-oct-2-ene (3). Fluorination of this at 200° gave fluorocarbon 10 . There was uncertainty about the stereochemistry of dodecafluoride 7 , but it turned out to be different from the product (4) of a palladium - catalysed hydrogenation of olefin 3 . Not only would stereoisomer 4 be expected to have its hydrogens cis from its synthesis, but its gas chromatographic retention time was greater than that of the fluorination product (7). In stereoisomeric pairs of 1H,2H- polyfluorocyclo-butanes [14], -pentanes [15], -hexanes [16] and -heptanes [17], the cis-isomer invariably has the longer retention time. Finally, fluorinations normally [12] give much more of a trans- than of a cis- isomer of this type: careful analytical gas chromatographic examination of the original fluorination product showed a very small peak with a retention time identical to that of the cis-isomer (4).

Because isolation of compounds 7 - 9 was relatively difficult, a mixture of the three was passed into molten alkali at 200° to give a readily separable mixture of the perfluoro-ene (3) and the 2H-2-ene (2). Cobalt trifluoride at 100° converted the latter to 9.

The olefinic mixture (2 + 3) was oxidised with potassium permanganate in acetone to give a fluoro-acid product (5), in which, after methylation with diazomethane, the dimethyl esters of difluoromalonic acid and tetrafluorosuccinic acid were identified. There was also a constituent which was probably dimethyl decafluorocyclohexane - 1,4- dicarboxylate. This result was expected: undecafluorocyclohexane carboxylic acid readily decarboxylates [18] to decafluorocyclohexene, and though hydrogen - containing fluorocyclohexane - 1,4 - dicarboxylic acids are more stable [1], the decafluoro - diacid would be expected to decompose to perfluorocyclohexa -1,3- and -1,4- diene, and thence to difluoromalonic and tetrafluorosuccinic acids in the oxidising medium.

The mixture 13 + 15 was obtained in fair quantity from the fluorination of 11 and was passed through molten KOH at 200° to give two olefinic products. One was the known [9] 1H-2-ene (20), arising from the dodecafluoride (15). The second olefin was a new compound, shown to be the 1H,3H-2-ene (18) and which came from the 1H,3H,3H-undecafluoride (13). The 1H,2H/3H- undeca- (12) and 1H,2H- dodeca- (14) fluorides were not isolated in sufficient quantity for dehydrofluorination individually, but a mixture of all four compounds (12 - 15) was passed through molten KOH at 210° and afforded, besides 20 and 18, the 1H,2H-2-ene (19), arising, together presumably with some of the isomer (18), from undecafluoride 12. The structures of 18 and 19 were clearly established from their nmr spectra; the 1H,3H- isomer (18) had an absorption due to the bridgehead fluorine at ca 211 p.p.m. and the 1H,2H- isomer (19) at 222 p.p.m. (cf. the other compounds with bridgehead fluorines both with and without hydrogen in an $\alpha$ - position — Tables 1 and 2).

The 1H,2H,4H- undecafluoride (29) also was dehydrofluorinated with molten alkali, to give a 1H,4H- ene (28) as shown by fluorination at 100° to the 1H,4H- dodecafluoride (30).

Though all of these dehydrofluorinations gave good yields of bicyclo-octenes, relatively forcing conditions were required. Qualitatively, they proceeded less readily than for monocyclic polyfluorides [14, 17] with $>$CHF or $>$CHF.CHF$<$ groupings.

The smooth hydrogenation of 3 to 4 is also significant; similar reactions on monocyclic perfluoro - enes have often given mixed products due to progressive hydrogenation, elimination of HF, further hydrogenation, and so on. Dehydrofluorinations from open-chain polyfluoroalkanes with >CHF and >CHF.CHF< groupings are also much slower [19] than from comparable monocyclic systems. In all these reactions, heterogeneous conditions are necessary synthetically, to prevent rapid nucleophilic attack on the olefinic products. It seems thus far that eliminations are slowest from open chain systems where free rotation is possible, and from the very rigid bicyclo-octane system. For polyfluorocyclo-butanes [14], -pentanes [15], and -heptanes [17] however, eliminations of hydrogen and fluorine arranged trans are rapid, and of those arranged cis are almost as ready. For polyfluorocyclohexanes [16], trans-arranged hydrogen and fluorine eliminate easily, but other arrangements less readily. Clearly, further exposition of the factors controlling these dehydrofluorination reactions is called for.

Replacement of bridgehead hydrogen- As shown by mass spectrometry, exchange of deuterium for hydrogen occurred with the 1H- (16) and the 1H,4H- compound (30) under heterogeneous conditions involving KOH in $D_2O$. Deuterium uptake into both compounds (16 and 30) occurred also using a homogenous non-basic system, deuterium oxide in hexadeuteroacetone. These preliminary observations have since been extended further [20] into a direct comparison of 1H-undecafluorobicyclo[2,2,1]heptane, compound 16, and tristrifluoromethylmethane.

The relative stability of the 1-lithio-derivative (21) permitted it to be prepared by exchange of 16 with methyl lithium at 18°, and it was converted into the trimethylsilane (26) and also to the known [9] 1-iodide (25), which formed a Grignard reagent (27), in diethyl ether, with some difficulty. Compound 27 on addition of water regenerated 16, whilst with acetaldehyde, a 1-(hydroxyethyl)-compound (32) was formed. This Grignard (27) was fairly stable in refluxing diethyl ether and not much decomposition had occurred after 20 hours; the products could not be identified.

The 1H- olefin (20) was found to react with an alkyl lithium (in this case the n-butyl was used) preferentially by metallation at the 1-position, rather than by the equally likely addition of the nucleophile to the double bond. Addition of iodine gave the unsaturated iodide (24), though a small amount of unidentified product could have arisen from addition.

Application to the 1H- compound (16) of an aqueous basic system (KOH/$H_2O$/DMSO or methanol) in the presence [5] of a nucleophile acceptor worked well in two cases: with methyl iodide, the known [9] 1-methyl derivative (22) was made in better yield than previously obtained via methyl lithium; with formaldehyde, the 1-hydroxymethyl- compound (17) was made. This last reaction was also applied to the 1H,4H-dodecafluoride (30), to give the 1,4-bis(hydroxymethyl)- derivative (31). Qualitatively, compounds 16 and 30 undergo these replacements at least as readily as the corresponding norbornanes.

It is of interest that acidity measurements [6] on the 1H- compound (16) showed that it is in fact significantly more acidic than any of the polyfluoronorbornanes. Exchange rates for deuterium are significantly greater for 16 than for the analogous norbornane [20].
Decomposition via a 'bridgehead olefin' - In the earlier work [9] virtually no decomposition of the 1-lithio-derivative (21) had occurred after an hour in refluxing ether. Accordingly, the monohydride (16) in solution in diethyl ether was treated with methyl lithium made from methyl iodide, and the system refluxed for 70 hours. The four components present were then isolated and identified, and the proportions in the mixture determined by analytical gas chromatography as the 1-iodide (25; 20%), 1H (16; 55%), the 1-iodo-2-ene (24; 5%) and the 1H-2-ene (20; 20%)[Scheme 2]. The mode of decomposition is similar to those postulated for the lithio-derivatives of 1H,4H- [4] and 1H,4-trifluoromethyl- [13] decafluoronorbornane. The basic pathway involves slow loss of lithium fluoride from the 1-lithio compound (21) to give [7,8] a transient reactive bridgehead 'olefin' (33). Back addition to this of lithium iodide (present in solution from the preparation of the methyl lithium from methyl iodide) affords a new lithio-derivative (34), which loses LiF to give product 24. Thus far, this is as for

1H-undecafluoronorbornane [7] but now, as with the more stable lithio-norbornanes mentioned above [4,13], the stability of the parent lithio-compound (21) means that an equilibrium can be established. This involves compounds 21, 24, 25 and the 1-lithio-2-ene (35). Addition of water at the end will give 16 and 20 from the undecomposed lithio-derivatives (21 and 35). In this case, despite the much longer reflux time, much of the starting material (16) was regenerated. This lithio-derivative (21) is the most stable saturated perfluoroalkyl lithium yet encountered, decomposing very much more slowly than the perfluoronorbornyl analogue, significantly more so than the 4H- and 4-$CF_3$- norbornyl species, and comparably to the 1-lithio- bicyclo[2,2,1]-hept-2-ene[21].

However, the geometry of the systems might be thought marginally to favour elimination from the bicyclo-octane since a slightly less strained 'bridgehead olefin' should be produced thereby. Nevertheless, even if correct, considerations such as these are clearly insignificant beside other unknown factors which must stabilise the perfluorobicyclo[2,2,2]octyl system, or maybe destabilize the perfluorobicyclo[2,2,1]heptyl one. Further work in this area is clearly merited.

## EXPERIMENTAL SECTION

### Techniques

Gas-Liquid Chromatography - For analytical work a Perkin Elmer Fractometer was used with a glass tube 2 m x 4 mm diameter packed with carbowax/celite 1:4 (Unit A). Semi-preparative work was done on a Pye 104 chromatograph with a tube 4.6 m x 6 mm packed with silicone gum/celite 1:5 (Unit B), and a tube 9.2 m x 6 mm packed with carbowax/chromosorb P 1:4 (Unit C). Input pressures were $H_2$ 10 p.s.i. ; $N_2$ 15 p.s.i. and air 15 p.s.i. Preparative separations were done in copper tubes 2 m x 25 mm packed with silicone gum/celite 1:4 (Unit D), and 4.88 m x 35 mm packed with carbowax/chromosorb P 1:4 (Unit E). Quoted for each separation are the unit used, operating temperature and nitrogen flow-rate (meter reading on the Perkin Elmer Fractometer, litres per hour for the preparative columns).

Fluorinations - These were all done in a small horizontal reactor [22] with a horizontal stirrer shaft and filled with cobalt trifluoride (ca. 100g). The inlet was a horizontal glass tube carrying a stopper through which starting materials (all solids) were introduced. These were then swept into the reactor by a stream of nitrogen whilst the inlet was warmed by a heating tape. Exit gases were passed over sodium fluoride pellets heated to 130 - 150°, and products were condensed in a glass trap at - 180°.

Melting points - All the fluorohydrocarbons made were volatile solids. Melting points were done in glass capilliary tubes sealed off to leave the minimum of free space above the sample.

Spectroscopy - Infrared spectra were measured on a Perkin Elmer 257 grating instrument with sodium chloride optics, mass spectra on an A.E.I. M.S.9.

## Fluorinations, dehydrofluorinations, characterisations

Fluorination of 1,2,3,4,5,5,6,6- Octafluorobicyclo[2,2,2]oct-2-ene (1) - The adduct (1) (9.6g) was sublimed into a nitrogen stream (3 $lh^{-1}$) during 30 min and passed through the reactor at 180°. The reactor was swept with nitrogen (5 $lh^{-1}$) for 1.5 h further, and the condensate (12.2g) analysed by g.l.c. (A, 100°, 4.5) showing 5 products; 10 (1%), 9 (27%), 8 (27%), 7 (33%), and 6 (12%). Separation of a batch (5.0g) by preparative g.l.c. (E, 80°; 20) into 5 fractions followed by a further separation of each under identical conditions afforded (i) tetradecafluorobicyclo[2,2,2]-octane (10) with a correct [9] ir spectrum: (ii) 2H-tridecafluorobicyclo[2,2,2]octane (9) nc, m.p. 182-3° (Found: C, 27.5; H, 0.5; F, 72.2. $C_8HF_{13}$ requires C, 27.9; H, 0.3; F, 71.8%); m/e 325 (M - 19), 275 (M - $CF_3$): (iii) 2H,2H-dodecafluorobicyclo-[2,2,2]octane (8) nc, m.p. 182° (Found: C, 29.5; H, 0.9; F, 69.1. $C_8H_2F_{12}$ requires C, 29.5; H, 0.6; F, 69.9%); m/e 326 (M), 307 (M - 19) : (iv) 2H/3H-dodecafluorobicyclo[2,2,2]-octane (7) nc, m.p. 184° (Found: C, 29.1; H, 0.8; F, 69.1%); m/e 326, 307: (v) 2H,2H,3H,3H- decafluorobicyclo[2,2,2]octane (6) nc, m.p. 203° (Found: C, 32.8; H, 1.3; F, 65.7. $C_8H_4F_{10}$ requires C, 33.1; H, 1.4; F, 65.5%); m/e 290 (M), 271 (M - 19).

Fluorinations of Products 6 - 9 - These were conducted at 320°, the compound sublimed in $N_2$ (3 $lh^{-1}$), the reactor then purged with $N_2$ (3 $lh^{-1}$) for 1.5 h, the products being separated by g.l.c. (E, 60°, 15) and identified by ir: 9 (1.0g) gave 10 (0.6g) and 9 (0.1g); 8 (0.6g) gave 10 (0.3g), 9 (0.1g) and 8 (trace); 7 (0.5g) gave 10 (0.3g), 9 (trace) and 7 (trace); 6 (1.0g) in 3 passes gave 10 (0.6g) and 9 (0.1g).

Dehydrofluorination of 2H- Tridecafluoride (9) - Compound 9 (1.7g) was sublimed into a nitrogen stream (10 $lh^{-1}$) which was bubbled through molten potassium hydroxide (250g) in a vertical tube kept at 200 - 210°. The nitrogen flow was continued for 15 min further, and the product, condensed in a trap at -180°, was dodecafluorobicyclo-[2,2,2]oct-2-ene (3) nc, (1.6g), m.p. 125 - 6°
(Found: C, 29.3; F, 70.4. $C_8F_{12}$ requires C, 29.6; F, 70.4%); m/e 324 (M), 305 (M - 19); ir 1765 $cm^{-1}$ (-CF=CF-).
When passed as above into the fluorination reactor at 200°, 3 (0.1g) afforded 10 (0.1g).

Hydrogenation of Dodecafluoro-2-ene (3) - Compound 3 (1.8g), palladium on charcoal (0.1g) and ethanol (110 $cm^3$) were shaken together in hydrogen at 1 atm. for 24 h, 130 $cm^3$ being taken up. After filtration, the solution was concentrated to 60 $cm^3$ by removal of solvent through a 6" vacuum-jacketed distillation column. Water (200 $cm^3$) was added to the residue, and the precipitate distilled from phosphoric oxide to give 2H,3H/- dodecafluorobicyclo-[2,2,2]octane (4) nc, (1.8g) m.p. 196° (Found: C, 29.8; H, 0.9; F, 69.7%).

2H-Undecafluorobicyclo[2,2,2]oct-2-ene (2) - A mixture (4.4g) of 7, 8 and 9 was dehydrofluorinated as above ($N_2$ stream continued for 25 min.) to give a product (4.1g). Separation of a portion (3.2g) by g.l.c. (E, 70°, 15) gave the perfluoro-2-ene (3) (1.5g ; correct ir ) and 2H- undecafluorobicyclo[2,2,2]oct-2-ene (2) nc, (1.0g), m.p. 122° (Found: C, 31.1; H, 0.6; F, 68.0. $C_8HF_{11}$ requires C, 31.4; H, 0.3; F, 68.3%), m/e 306 (M), 287 (M - 19) ; ir 3105 $cm^{-1}$ (=CH), 1690 $cm^{-1}$ (-CH=CF-).
Fluorination of 2 (0.2g) at 100° gave 9.

Oxidation of a Mixture of the Perfluoro - (3) and 2H-2-ene (2) - The mixed olefins (3.7g., made from 7, 8 and 9 as above) added dropwise to vigorously - stirred potassium permanganate (7.5g) in acetone (75 cm$^3$), caused refluxing. After being refluxed for 1 h further, the mixture was cooled, water (100 cm$^3$) and hydrochloric acid (15 cm$^3$ ; 4N) added, acetone evaporated off at ca 20 mm. pressure, and the residual liquid decolourised with SO$_2$. Continuous ether-extraction for 12 h, followed by drying and evaporation, left a viscous liquid acid mixture (5) which was treated with excess diazomethane in ether. After 18 h, filtration, evaporation and drying gave a clear viscous liquid (4.0g). G.l.c. (B, 110° ) showed 3 major and 9 minor peaks and the 3 major components were isolated. The ir and nmr spectra of the two largest showed them to be dimethyl difluoromalonate and dimethyl tetrafluorosuccinate. The third had ir and nmr spectra that would be anticipated for dimethyl decafluorocyclohexane-1,4- dicarboxylate, but insufficient was present for a complete identification.

## Fluorination of 1,2,3,5,5,6,6-Heptafluorobicyclo[2,2,2]oct-2-ene(11) -

Adduct 11 (3.0g) was fluorinated as for 1, but at 280°. The reactor was swept with nitrogen (3 lh$^{-1}$) for 1 h further and the condensate (3.6g) analysed by g.l.c. (A, 100°, 4.5) showing 7 products; 10 (1%), 9 (4%), 16 (51%), 15 + 13 (33%), 14 (4%), and 12 (7%). Separation of a batch (5.0g) by preparative g.l.c. (E, 95°, 15) gave 6 fractions, of which the first three were each separated again under identical conditions to give (i) 10; (ii) 9 (traces with correct ir spectra); (iii) 1H-tridecafluorobicyclo[2,2,2]octane [9] (16, correct ir ).
The last three fractions were further separated (E, 115°, 20) to give (iv) a mixture of 1H,3H,3H-undeca- (13) and 1H,3H-dodeca-fluorobicyclo[2,2,2]octane (15) ;
(v) 1H,2H-dodecafluorobicyclo[2,2,2]octane (14) nc, m.p. 188° (Found: C, 29.1; H, 0.8; F, 70.1%); m/e 326 (M), 307 (M - 19) :
(vi) 1H,2H/3H-undecafluorobicyclo[2,2,2]octane (12) nc, m.p. 185° (Found: C, 31.2; H, 1.1; F, 68.0. C$_8$H$_3$F$_{11}$ requires C, 31.2; H, 1.0; F, 67.8%); m/e 308 (M), 239 (M - CF$_3$).

Product 16 (1.2g) passed as before through molten KOH at 210 - 215° was recovered (1.0g).

## Characterisation of Mixed Product 13 and 15 - Spectroscopy.

The mixture of 13 and 15 (fraction (iv) above) had a $^{19}$F nmr spectrum (Table 2), ir and mass spectrum consistent with the presence of the 1H,3H-dodecafluoride (15) and the 1H,3H,3H-undecafluoride (13) in respective proportions of 7:3.

Dehydrofluorination. Fraction (iv) (2.5g) as before gave product (2.1g), g.l.c. separation of which (E, 70°, 15) afforded 1H-undecafluorobicyclo[2,2,2]-oct-2-ene [9] (20, correct ir) (1.0g), m.p. 111°, and 1H,3H-decafluorobicyclo[2,2,2]oct-2-ene (18) nc, (0.6g), m.p. 120° (Found : C, 33.4; H, 0.8; F, 65.9. $C_8H_2F_{10}$ requires C, 33.3; H, 0.7; F, 66.0%) ; m/e 288 (M), 269 (M - F) ; ir 3110 $cm^{-1}$ (=$\overset{|}{\mathrm{C}}$H) , 1690 $cm^{-1}$ (-CH=CF-).

Dehydrofluorination of a Mixture of Products 12 - 15 - A mixture of fractions (iv) - (vi) (above) (8.5g), as before gave product (6.3g), of which a portion (5.5g) was separated by g.l.c. (E, 85°, 18) into 20 (3.0g), 18 (0.9g), and 1H,2H-decafluorobicyclo[2,2,2]oct-2-ene (19) nc, (0.5g), m.p. 132° (Found: C, 33.2; H, 1.0; F, 66.4%); m/e 288 (M), 269 (M - F), 219 (M - $CF_3$) ; ir 3107 $cm^{-1}$ (=$\overset{|}{\mathrm{C}}$H) , 1690 $cm^{-1}$ (-CH=CF-)

Fluorination of 2,3,5,5,6,6-Hexafluorobicyclo[2,2,2]oct-2-ene (23) - Adduct 23 (2.0g) at 225° gave a solid (3.0g) : g.l.c. analysis (A, 120°, 4) showed 2 major products, and separation (E, 120°, 18) of a batch (5.4g) afforded (i) a mixture of 10 and 16 (0.3g) : (ii) 1H,4H-dodecafluorobicyclo[2,2,2]octane (30) nc, (2.4g), m.p. 181° (Found: C, 29.1 ; F, 69.3%); m/e 326 (M) , 307 (M - F) , 257 (M - $CF_3$) ; (iii) 1H,2H,4H-undecafluorobicyclo[2,2,2]octane (29) nc, (1.6g), (Found: C, 31.6; H, 0.7; F, 67.9%); m/e 289 (M - F), 239 (M - $CF_3$). Product 30 (0.13g) passed through molten KOH at 200-210° in a stream of $N_2$ (1.5 $lh^{-1}$) was recovered (0.10g).

Fluorinations of Products 29 and 30 - In separate experiments each (0.2g) in 2 passes gave 10 (0.1g) and 16 (0.5g).

Dehydrofluorination of the 1H,2H,4H-Compound (29) - A stream of nitrogen (1.5 $lh^{-1}$) carried 29 (0.6g) through molten KOH (100g) at 200 - 210°. Product (0.5g) was completely expelled after 30 min further and was 1H,4H-decafluorobicyclo[2,2,2]oct-2-ene (28) nc, (Found: C, 33.6; H, 0.7; F, 65.6%); m/e 288 (M), 269 (M - F), 219 (M - $CF_3$); ir 1756 $cm^{-1}$ (-CF=CF-).
Passage of 28 (0.2g) over $CoF_3$ at 100° gave 30 (0.2g, correct ir).

## Reactions at bridgehead positions

Deuteriations of the 1H-(16) and 1H,4H-compound (30) - Compound 16 (0.5g) was shaken in a sealed tube with potassium hydroxide (10.1g) and deuterium oxide (15.1g) at 100° for 6 h. The product isolated was shown by mass spectrometry to be 77% deuterated. In a similar system on a smaller scale, compound 30 afforded a mixture with the product ratio 2H : H/D : 2D = 100:88:84. Both compounds (16 and 30) had taken up deuterium after being kept in $D_2O/CD_3COCD_3$ mixtures (up to 20% $D_2O$ by vol.) for several hours, though no uptake into 1H-undeca- and 1H,4H-deca-fluorobicyclo[2,2,1]heptane could be detected.

1-(Trimethylsilyl)tridecafluorobicyclo[2,2,2]octane (26) - To the 1H-tridecafluoride (16) (2.5g) in dry diethyl ether (10 $cm^3$) stirred vigorously at 18° was added methyl lithium in diethyl ether (0.9 M; made from methyl iodide) until evolution of methane ceased (ca. 160 $cm^3$). After 10 min further, trimethylchlorosilane (2.0g) was added, a white precipitate forming. After 16 h, the solution was filtered, and ether distilled off through a 6" vacuum-jacketed column packed with glass helices to leave a residue (2.8g). Separation by g.l.c. (D, 100° , 3.0) gave (i) ether and starting material (16) (0.4g): (ii) 1-(trimethylsilyl)tridecafluorobicyclo[2,2,2]octane (26) nc, (1.6g), m.p. 97° (Found: C, 32.0; H, 2.2 ; F, 59.2. $C_{11}H_9F_{13}Si$ requires C, 31.7 ; H, 2.2 ; F, 59.3%); m/e 401 (M - $CH_3$).

Tridecafluorobicyclo[2,2,2]octan-1-yl Magnesium iodide (27) - The 1H-compound (16) treated with methyl lithium and then iodine at 18° gave the 1-iodide [9] (25) (ca 80%). Compound 25 (1.3g) in dry ether (10 $cm^3$) was added to magnesium turnings (0.2g) in dry ether (20 $cm^3$) a crystal of iodine added and the mixture refluxed for 2 h, a white precipitate being formed. Dilute $H_2SO_4$ (0.1N; 50 $cm^3$) was added and isolation involving g.l.c. (E, 90°, 15) gave the 1H-tridecafluoride (16) (0.65g) and the 1-iodo-analogue (25) (0.2g).

1-Iodide (25) (2.1g) was converted to the Grignard reagent (27) as above and dry acetaldehyde then added dropwise until a viscous yellow syrup began to be formed from it. The mixture was filtered, washed with HCl (1N, 10 $cm^3$) and water (2 x 10 $cm^3$), dried (Mg $SO_4$), and the ether distilled off through a 6" vacuum-jacketed column packed with glass helices. The residue by g.l.c. (B, 120° ) gave, besides ether, the 1H-compound (16) (0.2g) and 1-(1'-hydroxyethyl)tridecafluorobicyclo[2,2,2]octane (32) nc, (0.7g), m.p. 89° (Found: C, 31.0; H, 1.4; F, 63.8. $C_{10}H_5F_{13}O$ requires C, 30.9; H, 1.3; F, 63.6%); ir 3400 cm$^{-1}$ (broad) (-OH).

1-Iodoundecafluorobicyclo[2,2,2]oct-2-ene (24) - To a well-stirred solution of the 1H-2-ene (20) (6.0g) in diethyl ether (50 cm$^3$) was added n-butyl lithium in hexane until the evolution of butane ceased (ca. 450 cm$^3$). After 15 min, resublimed iodine (5.2g) was added and after a further 15 min, sodium thiosulphate (4.0g) in water (40 cm$^3$). After vigorous shaking the ether layer was separated, washed with water, dried (Mg $SO_4$), filtered and the ether distilled through a 6" column as before. The residue by g.l.c. (E, 110°, 17) gave, besides ether and hexane, (i) 1-iodoundecafluorobicyclo-[2,2,2]oct-2-ene (24) nc, (4.0g), a colourless liquid (Found: C, 22.5; F, 47.6. $C_8F_{11}I$ requires C, 22.2; F, 48.4%); m/e 432 (M), 363 (M - $CF_3$), 332 (M - $C_2F_4$) ; ir 1747 cm$^{-1}$ (-CF=CF-) : (ii) unidentified fluorine-containing products (0.2g).

1-Methyltridecafluorobicyclo[2,2,2]octane (22) - The 1H-compound (16) (2.0g) in dimethyl sulphoxide (5 cm$^3$) was added to vigorously-stirred KOH (1.9g) in DMSO (100 cm$^3$) and water (20 cm$^3$). After 45 min, methyl iodide (4.0 cm$^3$) was added and the mixture heated to 45°. A cloudy precipitate formed and sublimed into the reflux condenser, a process completed by the addition of water (170 cm$^3$) and heating the mixture to 90° for 90 min. The product was scraped from the condenser, mixed with phosphoric oxide and sublimed at room temperature under diminished pressure onto a cold finger to give the 1-methyl derivative (22), (1.8g), m.p. 192° (cited [9], 185 - 186°: identical ir).

1-(Hydroxymethyl)tridecafluorobicyclo[2,2,2]octane (17) - The 1H-compound (16) (0.8g) was added to well-stirred methanol (50 cm$^3$) and 40% aqueous formaldehyde (10 cm$^3$) containing KOH (0.5g). The mixture was refluxed for 6 h, stirred at 15° for 16 h further, acidified with conc. HCl to pH4 and fractionally distilled through a 6" column. The early distillates contained starting material (16) (0.8g). Addition of a little water to the residue (b.p. > 70°) precipitated an oil (0.6g) which crystallised in a desiccator. Sublimation at 100°/20 mm gave the 1-hydroxmethyl-compound (17) nc, (0.5g), m.p. 209 - 210° (Found: C, 29.2; H, 1.1; F, 66.2. $C_9H_3F_{13}O$ requires C, 28.9; H, 0.8; F, 66.0%); m/e 374 (M), 305 (M - $CF_3$), 274 (M - $C_2F_4$); ir 3320 $cm^{-1}$ (broad) (-OH).

1,4-Bis(hydroxymethyl)dodecafluorobicyclo[2,2,2]octane (31) - The 1H,4H-octane (30) (0.6g) in DMSO (5 $cm^3$) was added to vigorously-stirred KOH (2.2g) in 40% aqueous formaldehyde (15 $cm^3$) and DMSO (50 $cm^3$). After 30 min at 18°, water (100 $cm^3$) and conc. HCl (10 $cm^3$) were added and the solution ether-extracted. The ether solution was water-washed, dried (Mg $SO_4$), and evaporated to a pale yellow oil (0.9g) which crystallised in a desiccator. Recrystallisation from benzene afforded the diol (31) nc, (0.5g), m.p. 214° (Found: C, 31.5; H, 1.7; F, 58.9. $C_{10}H_6F_{12}O_2$ requires C, 31.1; H, 1.6; F, 59.0%); m/e 386 (M), 356 (M - $CH_2O$); ir 3320 $cm^{-1}$ (broad) (-OH).

Decomposition of 1-Lithiotridecafluorobicyclo[2,2,2]octane (21) - To a well-stirred solution of the 1H-compound (16) (4.4g) in ether (6 $cm^3$) at 18° was added an ethereal solution of methyl lithium (0.8M; prepared from methyl iodide). When approx. 16 $cm^3$ had been added, evolution of methane ceased (290 $cm^3$). The solution was stirred for 2 h at 18° then refluxed gently for 70 h. Water (9 $cm^3$) and dilute $H_2SO_4$ (4N, 2 $cm^3$) were added, the ether layer water-washed (2 x 10 $cm^3$), dried (Mg $SO_4$), and the ether distilled off through a 6" column. The residue (5.9g) by analytical g.l.c. (A, 88° and 160°, 4.2) contained a little ether and 4 components (below), isolated by g.l.c. (C, 60°). Owing to volatility, an accurate weight balance could not be achieved, but the relative proportions present were obtained by peak area comparisons. Present, (correct ir spectra) were 1H-undecafluorobicyclo[2,2,2]oct-2-ene (20) (20%); 1H-tridecafluorobicyclo[2,2,2]octane (16) (55%); 1-iodoundecafluorobicyclo-[2,2,2]oct-2-ene (24) (5%); 1-iodotridecafluorobicyclo[2,2,2]octane (25) (20%).

## $^{19}F$ NMR spectra

Fluorine magnetic resonance spectra were used to verify the structures of the compounds prepared. Spectra were obtained using a Varian XL 100 spectrometer at 94.1 MHz from solutions in deuterochloroform using fluorotrichloromethane as internal reference. Double irradiation at both $^{1}H$ and $^{19}F$ frequencies was carried out where appropriate in the assignment of signals. Where necessary for analysis, spectra were also run in a Perkin-Elmer R12B instrument at 56.4 MHz. Assignment of the $^{19}F$ spectra of the more symmetrical of these compounds is straightforward and follows the usual pattern for cyclic fluorocarbons:

(a) Ring $>CF_2$ resonances occur in the range 105-125 p.p.m. upfield of the reference. If the nuclei are non-equivalent their spectrum takes the general form of an AB quartet with an apparent geminal coupling of 240-270 Hz, each signal being broadened by unresolved smaller scale coupling. In the less symmetrical molecules these effects produce a complexity of signal which is not readily analysed. However, the deshielding effect associated with the introduction of hydrogen in adjacent ring positions is sufficient to separate the low-field half of the 'quartet' and measurement of this at two frequencies permits the evaluation of the chemical shifts. Analysis of the complex signals was therefore unnecessary in the elucidation of the molecular configuration.

(b) Bridgehead-F resonances are found at between 200 and 225 p.p.m.

(c) CHF signals occur in the same region as (b) but are readily distinguishable from the latter by their form of broadened doublets arising from a $J_{HF}$ of 40 to 50 Hz.

(d) Olefinic-F signals in the unsaturated compounds occur in the range 105 - 125 p.p.m.

The assignments given in Tables (1) and (2) are consistent both internally and with the chemistry involved and embody the correlation features detailed below.

### A Fluorobicyclo[2,2,2]oct-2-enes

Although the introduction of a double bond destroys the equivalence of the nuclei of the $>CF_2$ pairs of the saturated molecules, the resulting shielding difference is small (less than 4 p.p.m.) Likewise, replacement of a ring $>CF_2$ by $>CH_2$ has little effect on the shielding of other $>CF_2$ groups but it deshields the adjacent bridgehead-F by $\sim$23 p.p.m. and moves the olefinic-F signal upfield by $\sim$ 4 p.p.m. A bridgehead-H deshields both the adjacent olefinic-F and the adjacent $>CF_2$ by some 13 - 14 p.p.m. An olefinic-H deshields the remaining olefinic-F and the adjacent bridgehead-F by $\sim$34 and $\sim$14 p.p.m. respectively.

## B Fluorobicyclo[2,2,2]octanes

Substitution at the bridgehead by -H, $-CH_2OH$, $-SiMe_3$, -Me, deshields fluorine in adjacent ring positions without having any appreciable effect on shielding elsewhere in the molecule. More specifically, a bridgehead-H deshields an adjacent $>CF_2$ by $\sim$13 p.p.m. and a $>CH\underline{F}$ by $\sim$10 p.p.m. Introduction of a hydrogen into ring position 2, apart from moving the gem-F signal upfield by $\sim$94 p.p.m., deshields the adjacent bridgehead-F by $\sim$ 9 p.p.m. The effect of this substitution on the resonances of the fluorine nuclei attached to C(3) is to deshield the F cis to the H by $\sim$ 14 p.p.m. and to shield the F trans by $\sim$ 5 p.p.m. This effect, which serves to distinguish between cis and trans substitution at the 2 and 3 positions (compound 12), was deduced on the basis of the positive identification of the 2,3/- (cis) di-hydro compound (4) by virtue of its method of preparation. Substitution of both fluorine atoms by hydrogen at position 2 deshields the adjacent bridgehead-F by $\sim$17 p.p.m. and shields the gem-F pairs at positions 6 and 7 by $\sim$5 p.p.m. but results in no detectable separation of the latter into AB systems as might be anticipated by the loss of equivalence so introduced. As can be seen from the tabulated assignments, the substantial effects of hydrogen substitution on $^{19}F$ chemical shifts are virtually confined to those fluorine atoms on carbon atoms directly bonded to the substitution site and are approximately additive.

## ACKNOWLEDGEMENTS

The authors thank the British Petroleum Company for a maintenance award (to J.B.), Dr. J.R. Majer for the mass spectrometry, and Mr. M.S. Tolley for obtaining the nmr spectra.

## REFERENCES

1 Part II of this series; J. Battersby, R. Stephens, and J.C. Tatlow, J. Fluorine Chem., 9 (1977) 127.

2 F. Hardwick, A.E. Pedler, R. Stephens, and J.C. Tatlow, J. Fluorine Chem., 4 (1974) 9; and earlier papers cited therein.

3 S.F. Campbell, J.M. Leach, R. Stephens, and J.C. Tatlow, J. Fluorine Chem., 1 (1971/2) 85.

4 S.F. Campbell, J.M. Leach, R. Stephens, J.C. Tatlow, and K.N. Wood, J. Fluorine Chem., 1 (1971/2) 103.

5 P.J.N. Brown, R. Stephens, J.C. Tatlow, and J.R. Taylor, J. Chem. Soc. Perkin Trans. I, (1972) 937.

6 A. Streitwieser and D. Holtz, J. Amer. Chem. Soc., 89 (1967) 692; D. Holtz, Progress in Phys. Org. Chem. (Editors Streitwieser and Taft), 8 (1971) 1; A. Streitwieser, D. Holtz, G.R. Ziegler, J.O. Stoffer, M.L. Brokaw, and F. Guibé, J. Amer. Chem. Soc., 98 (1976) 5229.

7 S.F. Campbell, R. Stephens, and J.C. Tatlow, Tetrahedron, 21 (1965) 2997.

8 G.L. Buchanan, Chem. Soc. Reviews, 3 (1974) 41.

9 W.B. Hollyhead, R. Stephens, J.C. Tatlow, and W.T. Westwood, Tetrahedron, 25 (1969) 1777.

10 J. Battersby, R. Stephens, and J.C. Tatlow, Tetrahedron Letters, (1970) 5041.

11 M. Stacey and J.C. Tatlow, Advances in Fluorine Chemistry, Butterworths, London, 1 (1960) 166.

12 J. Burdon, T.M. Hodgins, R. Stephens, and J.C. Tatlow, J. Chem. Soc., (1965) 2382.

13 R. Stephens, J.C. Tatlow, and K.N. wood, J. Fluorine Chem., 1 (1971/2) 165.

14 G. Fuller and J.C. Tatlow, J. Chem. Soc., (1961) 3198.

15 R.J. Heitzman, C.R. Patrick, R. Stephens, and J.C. Tatlow, J. Chem. Soc., (1963) 281.

16 R.P. Smith and J.C. Tatlow, J. Chem. Soc., (1957) 2505.

17 J.A. Oliver, R. Stephens, and J.C. Tatlow, unpublished; J.A. Oliver, Ph.D. Thesis, University of Birmingham, 1965.

18 T.J. Brice and J.H. Simons, J. Amer. Chem. Soc., 73 (1951) 4016; 4017.

19 A.E. Pedler, R.C. Smith, and J.C. Tatlow, J. Fluorine Chem., 1 (1971/2) 337.

20 J.H. Sleigh, R. Stephens and J.C. Tatlow, J.Chem. Soc. Chem. Comm.,(1979) 921; J. Fluorine Chem., in the press.

21 S.F. Campbell, R. Stephens, J.C. Tatlow, and W.T. Westwood, J. Fluorine Chem., 1 (1971/2) 439.

22 A.B. Clayton, R. Stephens, and J.C. Tatlow, J. Chem. Soc., (1965) 7370.

23 J.A. Godsell, M. Stacey, and J.C. Tatlow, Tetrahedron, 2 (1958) 193; R. Stephens, J.C. Tatlow, and E.H. Wiseman, J. Chem. Soc., (1959) 148.