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POLYFLUOROBICYCLO(2,2,1)HEPTANES
PART II*. FURTHER DERIVATIVES MADE FROM 1*H*-UNDECAFLUOROBICYCLO(2,2,1)HEPTANE

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SUMMARY

1*H*-Undecafluorobicyclo(2,2,1)heptane has been lithiated with methyl-lithium in ether, and thence converted into a range of derivatives including 1-iodo-, 1-hydroxymethyl-, 1-carboxy- and 1-aceto-undecafluorobicyclo(2,2,1)-heptane. The latter reacts further to give α-(undecafluorobicyclo(2,2,1)heptan-1-yl)vinyl acetate. The iodide gave a Grignard reagent, the decomposition of which was studied, and a bis-mercurial. Bridgehead derivatives in this series are easily synthesised. The pyrolytic decarboxylation of anhydrous sodium undecafluorobicyclo(2,2,1)heptane-1-carboxylate and the decomposition of 1-lithio-undecafluorobicyclo(2,2,1)heptane have been studied, and the decomposition products correlated with transient bridgehead olefins.

INTRODUCTION

This paper describes extensions to our original work on highly-fluorinated norbornanes[1], and illustrates further the wide synthetic utility of 1*H*-undecafluorobicyclo(2,2,1) heptane (I).

RESULTS AND DISCUSSION

Lithium undecafluorobicyclo(2,2,1)heptyl (II) was generated from (I) and methyl-lithium in ether[1] and at —50° with iodine gave 1-iodo-undecafluorobicyclo-(2,2,1)heptane (III) (73 %). This was readily reduced back to the 1*H*-fluorocarbon (I) by lithium aluminium hydride in ether at 0° in agreement with the anticipated

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* For Part I, see ref. 1.

positive character of the iodine. If an S_n2 reaction occurs the displaced perfluorocarbanionic species would subsequently be protonated[2]. However, the absence of any products from an intermediate organometallic suggests a four-centred transition state.

As disclosed in a preliminary note[3], with activated magnesium in ether at low temperatures the iodide (III) gave a moderate yield of its Grignard reagent (IV) as indicated by hydrolysis to the 1*H*-fluorocarbon (I) (36 %). However, after 1 h at 35° with 1 mole of magnesium, (III) gave, after hydrolysis, 1-iodo-nonafluorobicyclo(2,2,1)hept-2-ene[1] (V) (45 %) and small amounts of 1*H*-fluorocarbon (I) and 1*H*-nonafluorobicyclo(2,2,1)hept-2-ene[1] (VI). After 4 h at 35° with an excess of magnesium, the iodide gave, after hydrolysis, only 1*H*-nonafluorobicyclo-(2,2,1)hept-2-ene (VI) (83 %). Similarly, 1-bromo-undecafluorobicyclo(2,2,1)-heptane[1] (VII), after 4 h at 35° with an excess of magnesium, gave the latter olefin (VI) (40 %). These observations can be rationalised in terms of an elimination of magnesium halogeno-fluoride from the Grignard reagent ((IV) or (VIII)) to give a transient bridgehead diradical* to which the addition of iodide or bromide rapidly occurs, and this is followed by a facile *β*-elimination to give the corresponding 1-halo-nonafluorobicyclo(2,2,1)hept-2-ene which is isolated when 1 mole of magnesium is used[3]. However, the unsaturated bridgehead halide can react in turn with magnesium, if an excess is present, to form the derived unsaturated Grignard reagent which is relatively stable[3] and which on hydrolysis is known to give the 1*H*-olefin (VI)[1].

The iodide (III) was susceptible to UV light and in the presence of mercury gave bis-(undecafluorobicyclo(2,2,1)heptan-1-yl)mercury (IX). However, there was no evidence for the formation of a dimer derived from the bridgehead radical, which would be expected to be very unstable (*cf.* ref. 4). Indeed, attempts to promote a reductive coupling of this iodide (III) with copper bronze failed, even after 72 h at 280°, giving a trace of the 1,*H*-fluorocarbon (I) and unchanged iodide. A similar reaction in the presence of iodopentafluorobenzene gave the same products in similar proportions together with a small amount of perfluorobiphenyl.

The lithio derivative (II), prepared as before, was treated at −50° with formaldehyde and with carbon dioxide to give 1-hydroxymethyl-undecafluorobicyclo(2,2,1)heptane (X) and undecafluorobicyclo(2,2,1)heptane-1-carboxylic acid (XI), respectively (both yields 90 %). The former, (X), characterised as its 3,5-dinitrobenzoate, was difficult to oxidise. Thus, potassium permanganate in 90 % aqueous acetic acid was without effect after 72 h at room temperature. However, sodium dichromate and concentrated sulphuric acid gave only a trace amount

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* Throughout this and the following two papers the terms " bridgehead olefin " and " bridgehead diradical " are used synonymously to describe a highly reactive intermediate (*cf.* for example, perfluorocyclohexyne, Campbell, Stephens and Tatlow, *Chem. Comm.*, (1967), 151, which could, although very strained, have some double-bond character or could be a true diradical.

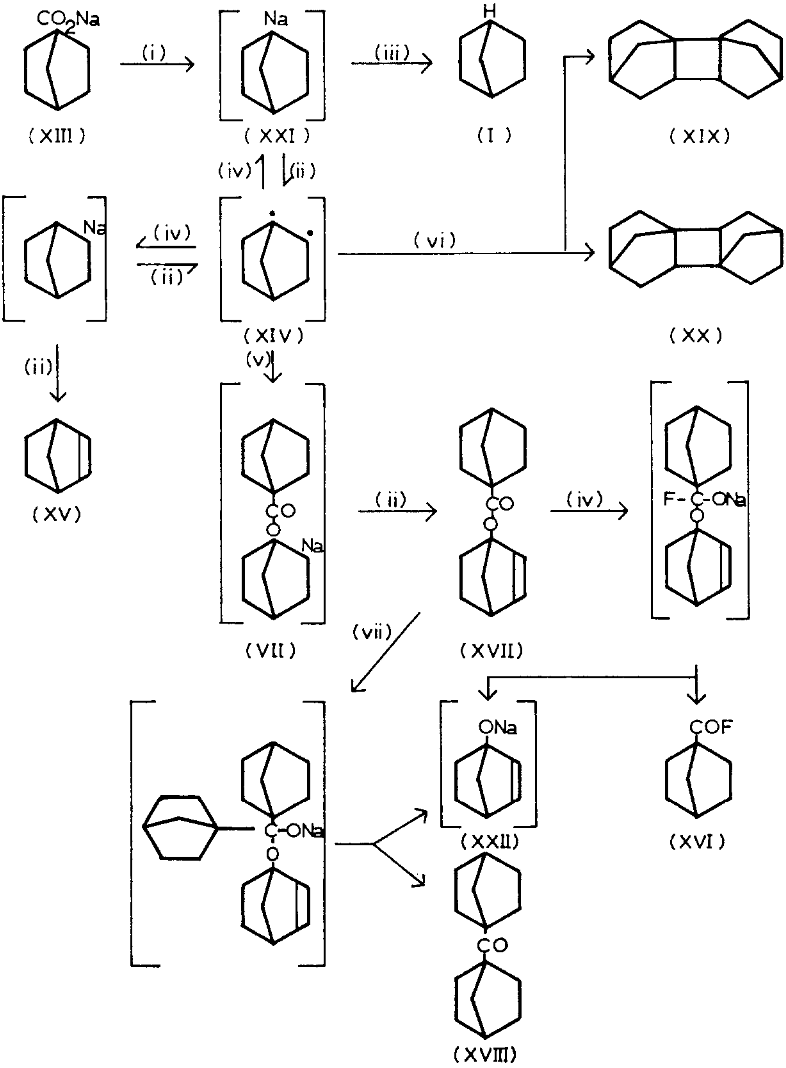
of the carboxylic acid (XI) and the suspected aldehyde (XII) (22 %) which was reduced by lithium aluminium hydride to the alcohol (X), and cleaved by aqueous alkali to give the 1*H*-fluorocarbon (I). In view of the poor carbon recovery from this oxidation it is likely that the acid (XI) is formed but decarboxylates to the very volatile 1*H*-fluorocarbon (I).

Undecafluorobicyclo(2,2,1)heptane-1-carboxylic acid (XI) gave an s-benzylthiuronium salt in the usual way, and with diazomethane in ether gave the methyl ester. The latter gave the 1-hydroxymethyl derivative (X) with lithium aluminium hydride in ether. Facile decarboxylation to the 1*H*-fluorocarbon prevented acid-catalysed esterification with ethanol at 100°. Such facile decarboxylation presumably reflects the stability of the derived bridgehead carbanion, which results from the direct inductive influence of the adjacent $>CF_2$ groups[1]. It is of interest to compare this behaviour with the much greater stabilities of the n-perfluoroalkane carboxylic acids, the much more difficult decarboxylations of which can be related to the lower stabilities of carbanionic centres directly attached to two or three fluorine atoms.

It has been suggested that the pyrolytic decarboxylation of an anhydrous sodium perfluoroalkane carboxylate to give an olefin involves a concerted β-elimination[5]. However, anhydrous lithium and sodium undecafluorobicyclo-(2,2,1)heptane-1-carboxylate readily decarboxylate and this suggests a non-concerted, carbanionic process, since the four-centred transition state cannot attain coplanarity.

The anhydrous total product from the carbonation of lithium undecafluorobicyclo(2,2,1)heptyl (II), generated using methyl-lithium produced from methyl bromide, was pyrolysed *in vacuo* to give 1-bromo-nonafluorobicyclo(2,2,1)hept-2-ene (XXVII), 1*H*-undecafluorobicyclo(2,2,1)heptane (I) and carbon dioxide. The first product presumably arises from a transient bridgehead olefin, or diradical[1], and the finely-dispersed lithium bromide; this performs a similar role in the solid phase at elevated temperatures to that which it takes in the decomposition of the organo-lithium in ethereal solution[1]. The isolation of the 1*H*-fluorocarbon (I) demonstrates the facility with which the intermediate lithio derivative (II) protonates.

The pyrolysis of pure anhydrous sodium undecafluorobicyclo(2,2,1)heptane-1-carboxylate (XIII) also gave a range of volatile products derivable from a transient bridgehead diradical (XIV), *viz.*, decafluorobicyclo(2,2,1)hept-2-ene (XV), undecafluorobicyclo(2,2,1)heptan-1-yl carbonyl fluoride (XVI), nonafluorobicyclo-(2,2,1)hept-2-en-1-yl undecafluorobicyclo(2,2,1)heptan-1-carboxylate (XVII), a trace of suspected bis-(undecafluorobicyclo(2,2,1)heptan-1-yl)ketone (XVIII) and a mixture of isomeric perfluoro-pentacyclo$[8,2,1^{1,10}, 1^{2,5}\ 0^{1,8}\ 0^{2,7}]$- and -$[8,2,1^{1,10}, 1^{4,7}\ 0^{1,8}\ 0^{2,7}]$- tetradecanes (XIX) and (XX), respectively. A tentative reaction scheme is set out in Figure 1. The sodio derivative (XXI), formed by loss of carbon dioxide from the sodium carboxylate (XIII), could enter into an equilibrium with the diradical (XIV) and sodium fluoride, and any "reverse" addition would result in the formation by a subsequent much easier *syn*-coplanar β-elimination of the highly volatile perfluoro olefin (XV), which would distil from the system and undergo no further reaction. The diradical (XIV) could also dimerise head-to-head or head-to-tail to give dimers (XIX) and (XX). (XIV) could also add unchanged sodium carboxylate (XIII) as depicted in Figure 1 and the sub-



(i) loss of CO_2; (ii) loss of NaF; (iii) H_2O; (iv) NaF; (v) $C_7F_{11}CO_2Na$; (vi) dimerisation; (vii) $C_7F_{11}Na$.

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

Fig. 1. Pyrolysis of sodium undecafluorobicyclo(2,2,1)heptane-1-carboxylate (XIII).

sequent *syn*-coplanar *β*-elimination of sodium fluoride would give the unsaturated ester (XVII). This could react further with sodium fluoride (*cf.* ref. 6), and with the sodium derivative (XXI), by additions across the carbonyl group to give adducts which could decompose to give the acid fluoride (XVI) and the ketone (XVIII), respectively. The unsaturated sodium alkoxide (XXII), a second product common to both reactions, should be involatile and may be partly responsible for the polymeric material found in the residue. The physical nature of this residue was not reproducible and varied between a highly viscous tar, and a brittle, glass-like solid. Other routes that could contribute to this involatile residue would arise from the "reverse" addition, to that depicted in Figure 1, of the sodium carboxylate (XIII) to the diradical (XIV).

As part of its characterisation, the highly-volatile crystalline olefin (XV) was fluorinated over cobaltic fluoride to give perfluorobicyclo(2,2,1)heptane. The acid fluoride (XVI) was hydrolysed to the carboxylic acid (XI) which was isolated as its s-benzylthiuronium salt. The ester (XVII) and lithium aluminium hydride in ether gave 1-hydroxymethyl-undecafluorobicyclo(2,2,1)heptane (X), but the anticipated second alcohol could not be isolated. The ketone (XVIII) was only detected by mass spectrometry as a contaminant in the crude dimer mixture ((XIX) and (XX)).

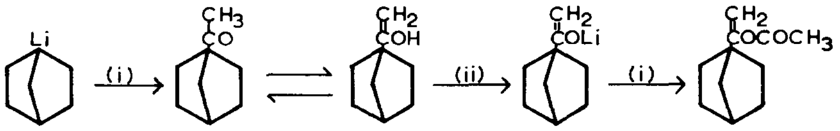
Although the formation of an ester by reaction of a carboxylate anion with an electron-deficient species, such as benzyne, is known[7], esters are not normally formed in the pyrolysis of perfluoro acid salts[6, 8] which give relatively unreactive olefins.

Pyrolysis of the anhydrous sodium carboxylate (XIII) in a stream of dry oxygen-free nitrogen gave a similar product distribution to that from the static pyrolysis, except for a marked diminution in the amount of the acid fluoride (XVI); this is consistent with the rapid removal of its postulated precursor, the ester (XVII). It was also of interest to observe that more of the dimers ((XIX) and (XX)) were formed in the early stages of the pyrolysis and more of the olefin (XV) in its later stages; this is consistent with the addition of sodium fluoride to the diradical (XIV). The polymeric material, obtained in the static decarboxylation, did not distil from the pyrolysis tube. At 340° a very rapid reaction deposited finely-divided carbon throughout the apparatus. A metallic mirror deposited on the pyrolysis tube burned quietly with a yellowish-green flame on contact with the atmosphere and reacted violently with water. The formation of sodium metal could result from the minor contribution of a high-temperature homolytic decarboxylation process, but it is surprising that it did not react with fluorocarbon products.

Lithium undecafluorobicyclo(2,2,1)heptyl (II) and an excess of acetyl chloride in ether gave a compound later identified as *α*-(undecafluorobicyclo-(2,2,1)heptan-1-yl) vinyl acetate (XXIII) (53 %) and the 1*H*-fluorocarbon (I) (27 %). With one mole of acetyl chloride, the lithiate (II) gave the vinyl acetate

(XXIII) (18 %), the 1*H*-fluorocarbon (I) (20 %) and the expected methyl undecafluorobicyclo(2,2,1)heptan-1-yl ketone (XXIV) (20 %). The acetate (XXIII) was reduced with lithium aluminium hydride to the ketone (XXIV) which did not give a 2,4-dinitrophenylhydrazone.

It seems that lithium undecafluorobicyclo(2,2,1)heptyl (II) abstracts a proton from the methyl undecafluorobicyclo(2,2,1)heptan-1-yl ketone (XXIV) already formed, preferentially in its enolic form, and the lithio derivative so produced reacts with more acetyl chloride as depicted in Figure 2.



(i) CH_3COCl ; (ii) $C_7F_{11}Li$

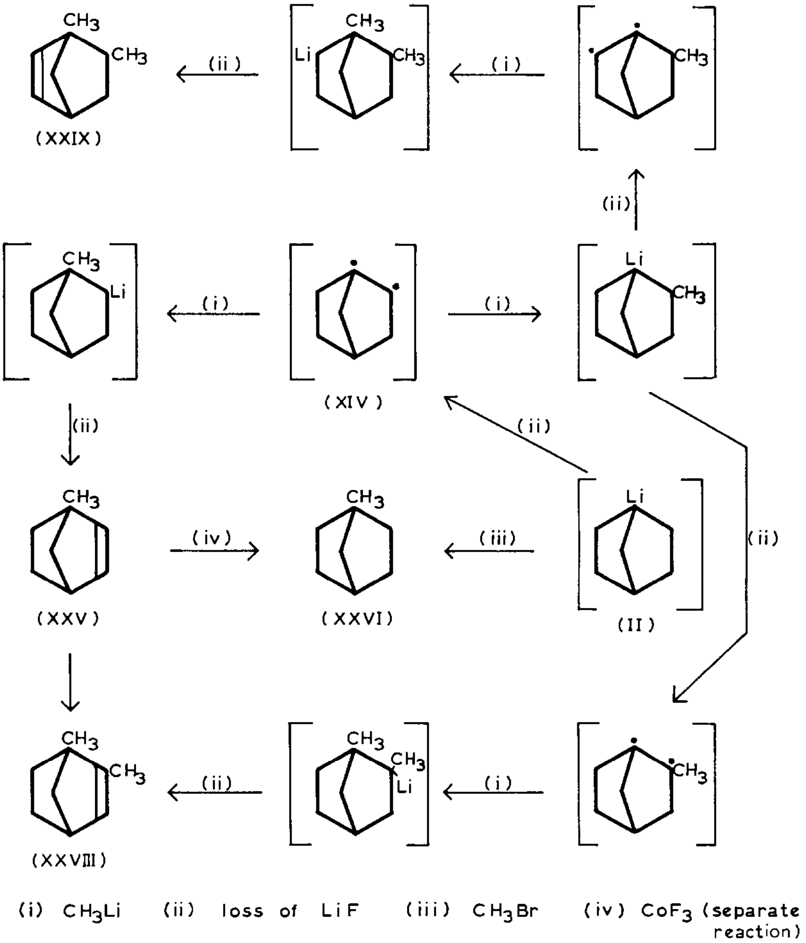
(All unmarked substituents are fluorine)

Fig. 2. Reaction of the lithiate (II) with acetyl chloride.

Such a scheme is supported by some reactions involving the closely-related 4*H*-lithio derivative described in the following paper. This two-stage process is unusual in a ketone synthesis, and reflects the electron-withdrawing power of the perfluoro group which makes the hydrogens more acidic.

Studies on the decomposition of lithium undecafluorobicyclo(2,2,1)heptyl (II) in ether have so far[1] been done in the presence of lithium iodide or lithium bromide, and have involved the additions of these species to the transient bridgehead diradical (XIV). Under these conditions only addition in one direction is effectively irreversible[1]. Therefore, it was of interest to allow decomposition to occur in the presence of methyl-lithium, since addition of this to the transient diradical in both directions would be effectively irreversible. When the lithium compound was allowed to decompose in the presence of 1 mole of methyl-lithium, made from methyl bromide, a complex mixture was obtained (see Figure 3). The most volatile component was shown by IR and NMR spectroscopy and mass spectrometry to be a mixture of 1-methyl-nonafluorobicyclo(2,2,1)hept-2-ene (XXV) and 1-methyl-undecafluorobicyclo(2,2,1)heptane (XXVI) in the ratio of 9:1, respectively. Fluorination of the mixture over cobaltic fluoride at 80° gave 1-methyl-undecafluorobicyclo(2,2,1)heptane (XXVI) (88 %) as the sole product. The second component was 1-bromo-nonafluorobicyclo(2,2,1)hept-2-ene[1] (XXVII). The third was shown by elemental analysis and mass spectrometry to have the molecular formula $C_9H_6F_8$, its IR spectrum contained a strong peak at 1710 cm^{-1}, ($-CF{=}C(CH_3)-$), and its ^1H NMR spectrum clearly indicated the presence of two types of methyl group. Hence, considering also its mode of formation

(Fig. 3), this olefin is 1,2-dimethyl-octafluorobicyclo(2,2,1)hept-2-ene (XXVIII). The last component also had the molecular formula $C_9H_6F_8$ as shown by elemental analysis and mass spectrometry, and its IR spectrum contained a peak at 1764 cm^{-1}, (–CF=CF–), with a small band at 1718 cm^{-1}, (–CF=C(CH$_3$)–) attributed to an impurity. The ^{1}H NMR spectrum revealed the presence of two types of methyl group such as would be present in 1,6-dimethyl-octafluorobicyclo-(2,2,1)hept-2-ene (XXIX), and the ^{19}F NMR spectrum was consistent with this structure. The latter also indicated the presence of two isomers consistent with an *exo-* and *endo-* position for the methyl group at C_6.



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

Fig. 3. Decomposition of the lithiate (II) in the presence of methyl-lithium.

When the 1-lithio-compound was allowed to decompose in the presence of 2 mole of methyl-lithium, only 1-methyl-nonafluoro- (XXV) and 1,2- and 1,6-dimethyl-octafluorobicyclo(2,2,1)hept-2-ene ((XXVIII) and (XXIX)) were obtained in the molar ratio of 4:37:11, respectively.

It is thus apparent that, as set out in Fig. 3, addition to the bridgehead diradical (XIV) occurs in both directions. However, the true proportion of nucleophilic attack at C_2 is difficult to assess since the ultimate product of attack at C_1 (XXV) may undergo further nucleophilic addition–elimination at C_2 to give the same 1,2-dimethyl olefin (XXVIII) as one possible product from the other mode of addition. Indeed, the poor carbon recovery in these decompositions, especially with 2 moles excess of methyl-lithium, suggests more extensive methyl substitution to give olefins of lower volatility. Nevertheless, the isolation of a 1,6-dimethyl olefin (XXIX) is unequivocal evidence for a substantial proportion of attack at C_2.

1-Bromo-nonafluorobicyclo(2,2,1)hept-2-ene (XXVII) must arise from the addition of lithium bromide to the diradical (XIV) formed after complete consumption of the more powerful nucleophile, for it is absent from the products of decomposition in the presence of two moles of methyl-lithium. Presumably the trace of the saturated 1-methyl compound (XXVI) arises from attack of (II) on some residual methyl bromide.

We believe that these highly-fluorinated bicyclic systems show many interesting features. Owing to the incipient acidity, and hence replacability, of the bridgehead hydrogens, many derivatives can be made. These include some whose analogues are not yet known in hydrocarbon chemistry, where similar approaches are not possible.

EXPERIMENTAL

Apparatus

Gas chromatography

Analytical work was carried out using 2 m glass columns (4 mm diam.) packed with silicone gum (SE 301)–celite (1:5), (col. H), tricresyl phosphate–celite (1:3) (col. I), dinonyl phthalate–celite (1:5) (col. L), dinonyl phthalate–celite (1:2) (col. P), silicone gum–celite (1:3.5) (col. Q), a 6 m glass column (4 mm diam) packed with dinonyl phthalate (1:10) (col. G), and a 1 m glass column packed with tricresyl phosphate–celite (1:3) (col. K). For preparative work copper columns (4.88 m long and 35 mm diam) were used packed with dinonyl phthalate–celite (1:5) (col. A), silicone gum–celite (1:5) (col. B), tricresyl phosphate–celite (1:3) (col. M), dinonyl phthalate–celite (1:2) (col. Q), and copper columns (4.88 m long and 75 mm diam) packed with silicone gum–celite (1:5) (col. C) and dinonyl phthalate–celite (1:5) (col. J). For semi-preparative work 2 m glass columns

(13 mm diam) were used packed with dinonyl phthalate–celite (1:2) (col. D), silicone gum–celite (1:2) (col. E), and tricresyl phosphate–celite (1:2) (col. F), and a 2 m copper tube (15 mm diam.) packed with dinonyl phthalate-celite (1:3) (col. N).

NMR spectroscopy

The proton and fluorine spectra were measured with a Varian HA-100 instrument at 94.1 Mcps with TMS and $CFCl_3$ as external references, and chemical shifts are quoted in ppm, except as otherwise stated.

Mass spectra

These were measured on an A.E.I. MS9 instrument.

Fluorination procedure

Fluorinations were carried out in the usual way (*cf.* ref. 9) in a stream of nitrogen (*ca.* 3 l/h) in a small stirred cobaltic fluoride reaction vessel made of nickel (48 cm × 5 cm diam.; it contained *ca.* 150 g of cobaltic fluoride).

Preparative

1-Iodo-undecafluorobicyclo(2,2,1)heptane (III)

To a well-stirred solution of 1*H*-undecafluorobicyclo(2,2,1)heptane (I) (5.2 g) in diethyl ether (85 ml) at −50°, an ethereal solution of methyl-lithium (0.78 *N*, from MeBr) was added drop-wise until the evolution of methane ceased (*ca.* 325 ml). Stirring was continued for 1 h at −50°, re-sublimed I_2 (5 g) in ether (40 ml) added slowly, and the stirred solution allowed to attain room temperature steadily during 4 h. Hydrated sodium thiosulphate (4 g) in water (50 ml) was then added, the ethereal layer separated, washed with water (2 × 30 ml), dried with $MgSO_4$, filtered, and most of the ether evaporated through a vacuum-jacketed column (15 cm) packed with glass helices. The residue (8.2 g) was separated by GLC (col. A, 100°; N_2, 17 l/h) to give: (i) ether (1.5 g); (ii) 1-iodo-undecafluorobicyclo(2,2,1)heptane (III) (nc) (5.5 g) m.p. 84–86° (sealed tube) (Found: C, 19.8; H, 0.0; I, 30.2. $C_7F_{11}I$ requires C, 20.0; I, 30.2 %).

Lithium aluminium hydride (0.45 g) was added slowly to a solution of the iodide (III) (0.92 g) in dry ether (40 ml) at 0°. The solution was kept for 12 h at room temperature with occasional stirring, cooled to 0° and hydrolysed by drop-wise addition of water (5 ml) and 4 *N* HCl (50 ml). The ethereal layer gave, in the usual way, a residue (1.4 g) which was separated by GLC (col. A; 80°; N_2, 17 l/h) to give ether and 1*H*-undecafluorobicyclo(2,2,1)heptane (I) (0.5 g) with a correct IR spectrum.

Undecafluorobicyclo(2,2,1)heptan-1-yl magnesium iodide (IV)

To a well-stirred suspension of magnesium turnings (0.3 g) and a crystal of iodine in ether (5 ml) at room temperature, ethyl bromide (0.3 ml) in ether

(10 ml) was added at a rate which maintained a gentle reflux. After stirring for 15 min at room temperature, the solution was cooled to $-50°$ and the 1-iodide (III) (0.8 g) in ether (15 ml) was added drop-wise. Stirring was continued for 2 h at $-50°$ and for a further 4 h while the solution warmed steadily to $-20°$, when water (50 ml) was added with vigorous stirring. The ethereal layer was treated in the standard manner and the residue (3.7 g) was separated by GLC (col. A; 90°; N_2, 16 l/h) to give: (i) ether; (ii) 1*H*-undecafluorobicyclo(2,2,1)heptane (I) (0.2 g); (iii) 1-iodo-undecafluorobicyclo(2,2,1)heptane (III) (0.4 g); all had correct IR spectra.

Decomposition of undecafluorobicyclo(2,2,1)heptan-1-yl magnesium iodide (IV)

1-Iodo-undecafluorobicyclo(2,2,1)heptane (III) (1.0 g) in ether (15 ml) was added drop-wise to magnesium turnings (0.05 g) and a crystal of iodine in gently refluxing ether (15 ml). The magnesium was completely consumed and a granular white ppt. had formed after 1 h. 4 *N* HCl (25 ml) was then added slowly to the solution stirred at 0°, and the ethereal layer treated as before to leave a residue, which was separated by GLC (col. A; 100°; N_2, 15 l/h) to give three fractions. Fraction (i) was ether and two other components (trace amounts). From their GLC retention volumes (col. G; 100°; N_2, 1.2 l/h) these were identified as 1*H*-nonafluorobicyclo(2,2,1)hept-2-ene (VI) and 1*H*-undecafluorobicyclo-(2,2,1)heptane (I). Fraction (ii) was 1-iodo-nonafluorobicyclo(2,2,1)hept-2-ene (V) (0.4 g) with a correct IR spectrum[1], and fraction (iii) was 1-iodo-undecafluorobicyclo(2,2,1)heptane (III) (0.2 g) with a correct IR spectrum.

The aqueous washings were evaporated to dryness, dissolved in glacial acetic acid and gave a positive test for fluoride ion on addition of cerous nitrate solution.

1-Iodo-undecafluorobicyclo(2,2,1)heptane (III) (1.0 g) in ether (15 ml) was added drop-wise during 1 h to magnesium turnings (0.2 g) and a crystal of iodine in refluxing ether (15 ml). The solution was refluxed for 4 h then decanted from unreacted magnesium, cooled to 0° and 0.1 *N* H_2SO_4 (40 ml) added. After separation, treatment of the ethereal layer in the usual way gave a residue which was separated by GLC (col. D; 72°; N_2, 7 l/h) to give ether and 1*H*-nonafluorobicyclo-(2,2,1)hept-2-ene (VI) (0.5 g) with a correct IR spectrum[1].

Preparation and decomposition of undecafluorobicyclo(2,2,1)heptan-1-yl magnesium bromide (VIII) in the presence of an excess of magnesium

1-Bromo-undecafluorobicyclo(2,2,1)heptane (VII)[1] (1.5 g) in dry ether (25 ml) was added drop-wise during 1 h to magnesium turnings (0.3 g) and a crystal of iodine in refluxing ether (10 ml). The solution was refluxed for 4 h then decanted from unreacted magnesium, cooled to 0° and 4 *N* HCl (30 ml) added. Treatment of the ethereal layer as before gave a residue (5.5 g) which was separated by GLC (col. A; 58°; N_2, 18 l/h) to give ether (3.4 g) and 1*H*-nonafluorobicyclo-(2,2,1)hept-2-ene (VI) (0.4 g) with a correct IR spectrum.

Bis-(undecafluorobicyclo(2,2,1)heptan-1-yl)mercury (IX)

1-Iodo-undecafluorobicyclo(2,2,1)heptane (III) (0.5 g) and re-distilled mercury (4 g) were shaken together under dry N_2 for 50 h in a stoppered silica flask placed in a wide range UV beam from a "Hanovia" lamp. The product (0.4 g) was sublimed from mercuric iodide and re-crystallised from CCl_4 to give bis-(undecafluorobicyclo(2,2,1)heptan-1-yl)mercury (IX) (nc) (*ca.* 0.1 g) m.p. 131–132° (Found: C, 21.0; H, 0.0. $C_{14}F_{22}Hg$ requires C, 21.4%), *m/e* 786 ($C_{14}F_{22}Hg$) and 620 ($C_7F_{11}Hg$ I).

1-Hydroxymethylundecafluorobicyclo(2,2,1)heptane (X)

1*H*-Undecafluorobicyclo(2,2,1)heptane (I) (6.0 g) and methyl-lithium (0.68 *N* from MeBr) in ether were mixed as before. Paraformaldehyde (2.0 g) was depolymerised at 180° and the formaldehyde carried by N_2 (2.5 l/h) to the solution so obtained. A wide-bore air leak led the formaldehyde above the surface of the solution, which was stirred vigorously at −60°. When all the paraformaldehyde had depolymerised, the stirred solution was allowed to warm steadily during 12 h to 0°, 4 *N* HCl (100 ml) added and the solution stirred for ½ h. The ethereal layer gave, in the usual way, a crystalline solid (6.4 g) a part (*ca.* 0.1 g) of which was sublimed (100°, 14 mm) to give 1-hydroxymethylundecafluorobicyclo(2,2,1)heptane (X) (nc) (*ca.* 0.1 g) m.p. 161° (sealed tube) (Found: C, 30.0; H, 0.6. $C_8H_3F_{11}O$ requires C, 29.6; H, 0.9%), $\nu_{max.}$ 3290 cm^{-1} (-OH), *m/e* 324 ($C_8H_3F_{11}O$), the ^1H NMR spectrum in CCl_4 consisted of a triplet (-OH) and a doublet (*J* 5.5 cps, $\rangle CH_2$) centred at 5.2 and 4.4 in the relative intensity ratio of 1:2, respectively.

3,5-Dinitrobenzoyl chloride (10 g) in benzene (5 ml) and alcohol (X) (0.5 g) in pyridine (1 ml) gave undecafluorobicyclo(2,2,1)heptan-1-yl methyl 3,5-dinitrobenzoate (nc) (0.6 g) m.p. 138.5–139.5° (from benzene) (Found: C, 34.6; H, 1.2. $C_{15}H_5F_{11}N_2O_6$ requires C, 34.7; H, 1.0%).

Sodium dichromate (6 g), concentrated sulphuric acid (30 ml) and the alcohol (X) (5.0 g) were stirred together at 100° for ½ h. The mixture was cooled, poured on to ice and extracted with ether for 60 h. The ether extract gave, in the usual way, the hygroscopic suspected undecafluorobicyclo(2,2,1)heptan-1-al (XII) (1.1 g) m.p. 96–97° (Found: C, 30.4; H, 0.7; F, 63.6. $C_8HF_{11}O$ requires C, 29.8; H, 0.3; F, 64.9%), $\nu_{max.}$ 1770 cm^{-1}. The aldehyde (XII) (0.2 g) and lithium aluminium hydride (0.15 g) in ether (10 ml) at 0° afforded 1-hydroxymethylundecafluorobicyclo(2,2,1)heptane (X) (0.13 g) with a correct IR spectrum. The aldehyde (XII) (0.5 g) and NaOH (2 g) in water (18 ml) were shaken together in a sealed tube at 100° for 1½ h to afford 1*H*-undecafluorobicyclo(2,2,1)heptane (I) with a correct IR spectrum.

Undecafluorobicyclo(2,2,1)heptane-1-carboxylic acid (XI)

1*H*-Undecafluorobicyclo(2,2,1)heptane (I) (10.0 g) and methyl-lithium (1.1 *N* from MeBr) in ether were mixed as usual and carbon dioxide, generated by sublimation of "Drikold" at room temperature and dried by passage through silica gel and phosphoric oxide, was bubbled into the stirred solution at −60° for 4 h. After warming to room temperature, stirring was continued for 12 h, then 4 *N* HCl (70 ml) was added, the ethereal layer separated and treated as usual to give a viscous liquid from which the last traces of ether were removed *in vacuo* to leave white flakes (9.8 g) which were sublimed (75°, 14 mm) to give undecafluorobicyclo(2,2,1)heptane-1-carboxylic acid (XI) (nc) (7.5 g) m.p. 84–86° (Found: C, 28.6; H, 0.3. $C_8HF_{11}O_2$ requires C, 28.4; H, 0.3 %), $\nu_{max.}$ *ca.* 3130 (hydrogen-bonded OH) and 1752 cm^{-1} ($\rangle C{=}O$), *m/e* 338 ($C_8HF_{11}O_2$) and a consistent fragmentation pattern with an intense fragment ion at 45 (CO_2H).

s-Benzylthiuronium chloride and the acid in water gave s-benzylthiuronium undecafluorobicyclo(2,2,1)heptane-1-carboxylate (nc) m.p. 85–86° (decomp.) (Found: C, 38.0; H, 2.4. $C_{16}H_{11}F_{11}N_2O_2S$ requires C, 38.1; H, 2.2 %).

An ethereal solution of diazomethane, prepared by addition of an ethanolic solution of KOH to *N*-methyl-*N*-nitroso-*p*-toluene sulphonamide in ether, was added drop-wise to a stirred solution of undecafluorobicyclo(2,2,1)heptan-1-carboxylic acid (XI) (1.0 g) in dry ether (15 ml) at 0° until effervescence ceased. The flask was left unstoppered for 12 h to remove excess diazomethane, and ether was evaporated *in vacuo* and the liquid residue (2.6 g) separated by GLC (col. A; 100°; N_2, 18 l/h) to give: (i) ether and ethanol (1.4 g); (ii) 1*H*-undecafluorobicyclo-(2,2,1)heptane (trace amount); (iii) methyl undecafluorobicyclo(2,2,1)heptan-1-carboxylate (nc) (0.7 g) m.p. 29.5–30° (Found: C, 30.4; H, 1.0. $C_9H_3F_{11}O_2$ requires C, 30.7; H, 0.9 %), $\nu_{max.}$ 1770 cm^{-1} ($\rangle C{=}O$), *m/e* 352 ($C_9H_3F_{11}O_2$) and a consistent fragmentation pattern with intense fragments at 294 (C_7HF_{11}), 59 (CO_2CH_3) and 15 (CH_3); the ^1H NMR spectrum of a solution in CCl_4 consisted of a sharp singlet at 4.1.

The methyl ester (0.1 g) and lithium aluminium hydride (0.1 g) in ether (5 ml) at 0° afforded undecafluorobicyclo(2,2,1)heptan-1-yl methanol (X) (0.05 g) with a correct GLC retention volume and IR spectrum.

Pyrolysis of lithium undecafluorobicyclo(2,2,1)heptan-1-carboxylate in the presence of lithium bromide

1*H*-Undecafluorobicyclo(2,2,1)heptane (I) (2.7 g) and methyl-lithium (1.1 *N* from MeBr) in ether were mixed in the usual way and carbon dioxide was bubbled into the solution, as before, for 2 h, during which the solution attained room temperature. The flask was kept in a "dry box" until most of the ether had evaporated.

The residue was transferred to a "Pyrex" glass "Y-piece" fitted with ground glass joints and two-way tap; this was then removed from the "dry box" and the residual ether evaporated *in vacuo* (0.1 mm). The residue was heated to 230° *in vacuo* on an oil bath and further pyrolysed with a Bunsen burner. The most volatile fraction (b.p. $<$−50°, 0.5 mm) was CO_2, with a correct IR spectrum. The liquid pyrolysate, after evaporation of CO_2, was shown by GLC (col. G; 100°;

N_2, 1 l/h and col. I; 102°; N_2, 2 l/h) to contain two components, which were separated on a semi-preparative scale (col. D; 88°; N_2, 4.3 l/h) to give 1-bromo-nonafluorobicyclo(2,2,1)hept-2-ene (XXVII) (0.2 g) and 1*H*-undecafluorobicyclo(2,2,1)heptane (I) (0.1 g), both with correct IR spectra. The charred residue from the pyrolysis was insoluble in a wide range of solvents and was not examined further.

Preparation and pyrolysis of anhydrous sodium undecafluorobicyclo(2,2,1)heptane-1-carboxylate (XIII) [with K. N. Wood]

Because of the hygroscopic nature of the title compound its preparation was always carried out in a Gallenkamp Manipulator Glove Box which was charged daily with phosphoric oxide. All apparatus was dried at 100° for several hours before being placed in the "dry box", together with reagents, several days prior to an experiment. The following manipulations were then conducted in the dry system. To a solution of undecafluorobicyclo(2,2,1)heptane-1-carboxylic acid (XI) (7.5 g; sublimed (14 mm) from P_2O_5) in dry ether (50 ml), sodium hydride was added slowly until hydrogen evolution ceased. The ethereal layer was decanted from the copious crystalline ppt. produced, and the pyrolysis apparatus (see earlier) charged with a small portion of the ppt. and removed from the "dry box". The last traces of ether were then evaporated *in vacuo* (0.1 mm) to leave a fine powder. The pyrolysis apparatus was then returned to the "dry box" and a sample of sodium undecafluorobicyclo(2,2,1)heptan-1-carboxylate (nc) removed for IR spectroscopy and elemental analysis (Found: C, 26.5; H, 0.0. $C_8F_{11}NaO_2$ requires C, 26.7 %).

A portion (4.7 g) of the sodium salt, placed into the pyrolysis apparatus in the same way and then removed from the "dry box", was heated *in vacuo* (0.1 mm) to a final temperature of 230°. The most volatile fraction of the pyrolysate (b.p. $<-50°$, 0.1 mm) was CO_2, with a correct IR spectrum. The liquid pyrolysate (2.0 g) was shown by GLC (col. G; 100°; N_2, 1 l/h; col. I; 78°; N_2, 3.2 l/h) to contain at least six components.

The total liquid pyrolysate (3.4 g) from two similar pyrolyses was separated by GLC (col. D; 89°; N_2, 4 l/h) to give 4 fractions. Fraction (i) was a mixture (0.4 g) and fraction (ii) was 1H-undecafluorobicyclo(2,2,1)heptane (I) (0.4 g), with a correct IR spectrum. Fraction (iii) was nonafluorobicyclo(2,2,1)hept-2-en-1-yl undecafluorobicyclo(2,2,1)heptan-1-carboxylate (XVII) (nc) (0.2 g), m.p. 56–57° (Found: C, 30.4; H, 0.3. $C_{15}F_{20}O_2$ requires C, 30.4 %), $\nu_{max.}$ 1814 ($>C=O$), and 1757 cm^{-1} ($-CF=CF-$), *m/e* 573 ($C_{15}F_{19}O_2$) and 321 ($C_8F_{11}O$); the ester (XVII) (0.05 g) and lithium aluminium hydride in ether at 0° gave undecafluorobicyclo(2,2,1)heptan-1-yl methanol (X), with a correct IR spectrum, and a volatile component which could not be isolated. Fraction (iv) was a mixture of the suspected decafluoronorbornyl-1,2-dimers ((XIX) and (XX)) containing a trace of di(undecafluoronorbornyl)ketone (XVIII) as shown by mass spectrometry. Re-separation of (iv) (col. F; 72°; N_2, 6.5 l/h) gave a mixture of the suspected perfluoropentacyclo-$[8,2,1^{1,10}, 1^{2,5}, 0^{1,8}, 0^{2,7}]$- (XIX) and -$[8,2,1^{1,10}, 1^{4,7}, 0^{1,8}, 0^{2,7}]$- (XX) tetradecanes (0.9 g). The IR spectrum was transparent in the region 2000–1600 cm^{-1} (saturated fluorocarbon), *m/e* 548 ($C_{14}F_{20}$), the ^{19}F NMR spectrum was very complex but contained two sharp singlets at 222.0 and 222.3 (bridgehead fluorines) and two broad singlets at slightly lower field (tertiary fluorines). Fraction (i) was dissolved in dry (Na) benzene and separated, (col. D; 52°; N_2, 4.5 l/h) to give two compounds; the first (i)(a) was decafluorobicyclo(2,2,1)hept-2-ene (XV) (nc) (0.2 g) m.p. 32–33°, $\nu_{max.}$ 1762 cm^{-1} ($-CF{=}CF-$), *m/e* 274 (C_7F_{10}) and a consistent fragmentation pattern. Its ^{19}F NMR spectrum in CCl_4 consisted of a doublet centred at 125.6 (J = 1 cps,$>CF_2$), a doublet centred at 137.9 (J = 18.2 cps, bridge $>CF_2$), a singlet at 148.9 ($\geqslant C-F$), and a singlet at 222.9 (bridgehead fluorine), in the relative intensity ratio of 2:1:1:1, respectively. This olefin (XV) (0.1 g) was sublimed in a stream of N_2 (5 l/h) and passed over CoF_3 (150 g) at 140° to give perfluorobicyclo(2,2,1)heptane (0.1 g) with a correct IR spectrum. The second sub-fraction (i)(b) was undecafluorobicyclo(2,2,1)heptan-1-yl carbonyl fluoride (XVI) (nc) (trace amount), $\nu_{max.}$ 1878 cm^{-1} ($>C{=}O$), *m/e* 321 ($C_8F_{11}O$), 293 (C_7F_{11}) and 47 (COF); this acid fluoride and water gave undecafluorobicyclo(2,2,1)heptane-1-carboxylic acid (XI) which was isolated as its s-benzylthiuronium salt.

When the pyrolysis mixture was heated above 230° a deep red highly-viscous liquid $\nu_{max.}$ 1800–1650 cm^{-1} ($-CF{=}CF-$ and/or $>C{=}O$) was obtained and a powdery residue which was not investigated further.

Flow pyrolysis [with K. N. Wood]

In a "dry box", sodium undecafluorobicyclo(2,2,1)heptan-1-carboxylate (XIII) (10.0 g) was spread uniformly in a glass tube (40 cm × 2.5 cm diam.). The tube was then placed in a cold oven and nitrogen (1.5 l/h, dried by passage successively through concentrated H_2SO_4, potassium hydroxide pellets, silica gel and magnesium perchlorate) passed through it. While the temperature was slowly raised the pyrolysates formed at 100–200° and 200–250° were collected at −180°, and GLC analysis (col. L; 100°; N_2, 4.5 l/h) revealed a greater proportion of the fluorocarbon dimers in the former, and a greater proportion of decafluorobicyclo(2,2,1)hept-2-ene in the latter. The combined pyrolysates (4.1 g) were separated by GLC (col. N; 90°; N_2, 3.5 l/h) to give: (i) decafluorobicyclo(2,2,1)-hept-2-ene (XV) (0.4 g) containing a trace of undecafluorobicyclo(2,2,1)hept-1-yl carbonyl fluoride (XVI); (ii) 1*H*-undecafluorobicyclo(2,2,1)heptane (I) (0.3 g); (iii) nonafluorobicyclo(2,2,1)hept-2-en-1-yl undecafluorobicyclo(2,2,1)heptan-1-carboxylate (XVII) (0.2 g); (iv) a mixture of the perfluorocarbon dimers ((XIX) and (XX)) (0.8 g); (v) suspected di(undecafluoronorbornyl)ketone (XVIII) (0.2 g), $\nu_{max.}$ 1765 cm^{-1}; (i)–(iv) had correct IR spectra. At 340° a very rapid reaction caused finely divided carbon to be dispersed throughout the system. The cooled pyrolysis tybe was found to be uniformly coated with a highly pyrophoric metallic mirror.

α-(Undecafluorobicyclo(2,2,1)heptan-1-yl)vinyl acetate (XXIII)

$1H$-Undecafluorobicyclo(2,2,1)heptane (I) (3.0 g) and methyl lithium (1.2 *N* from MeBr) in ether were mixed as usual and re-distilled acetyl chloride (10 ml) added drop-wise, the solution stirred for 2 h at −60° and then for a further 18 h while steadily attaining room temperature. At −5° a white ppt. formed. The solution was washed several times with water and the ethereal layer gave, in the usual way, a residue (7.9 g), which was separated by GLC (col. B; 125°; N_2, 20 l/h) to give: (i) a mixture (3.8 g); (ii) a mixture containing a trace of acetic acid which was removed by distillation *in vacuo* from soda lime to give α-(undecafluorobicyclo(2,2,1)heptan-1-yl)vinyl acetate (XXIII) (nc) (1.0 g) b.p. 177–178° (Found: C, 34.9; H, 1.3. $C_{11}H_5F_{11}O_2$ requires C, 34.9; H, 1.3%), $\nu_{max.}$ 1748 (s) ($\rangle C{=}O$) and 1657 (w) cm^{-1} ($\rangle C{=}CH_2$), *m/e* 378 ($C_{11}H_5F_{11}O_2$); its ^1H NMR spectrum consisted of a singlet at 1.9 (CH_3) and a quadruplet at 5.3 ($\gg CH$) in the relative intensity ratio of 3:2, respectively. The ester (XXIII) (1.9 g) and lithium aluminium hydride (0.12 g) in ether at 0° gave a liquid (2.6 g) which was separated by GLC (col. C; 80°; N_2, 4 l/h) to give ether (1.3 g) and methyl undecafluorobicyclo(2,2,1)heptan-1-yl ketone (XXIV) (0.3 g) with a correct IR spectrum. Fraction (i) was re-separated (col. A; 90°; N_2, 15 l/h) to give: (i)(a) ether, (i)(b) $1H$-undecafluorobicyclo(2,2,1)heptane (0.8 g) with a correct IR spectrum; (i)(c) acetic acid.

Methyl undecafluorobicyclo(2,2,1)heptan-1-yl ketone (XXIV)

$1H$-Undecafluorobicyclo(2,2,1)heptane (3.0 g) was converted to the lithium derivative in the usual way and freshly distilled acetyl chloride (0.8 ml; 1 mole) added and the solution allowed to attain room temperature. The ethereal layer, in the usual way, gave a residue (7.2 g) which was separated by GLC (col. B; 85°; N_2, 12 l/h) to give three fractions. Fraction (i) was a mixture (3.5 g) and (ii) was methyl undecafluorobicyclo(2,2,1)heptan-1-yl ketone (XXIV) (nc) (0.6 g) m.p. 38–39° (sealed tube) (Found: C, 32.0; H, 0.8. $C_9H_3F_{11}O$ requires C, 32.1; H, 0.9%), $\nu_{max.}$ 1744 cm^{-1} ($\rangle C{=}O$), *m/e* 336 ($C_9H_3F_{11}O$); its ^1H NMR spectrum in CCl_4 consisted of a singlet at 2.1 (CH_3). Fraction (iii) was α-(undecafluorobicyclo(2,2,1)heptan-1-yl)vinyl acetate (0.7 g) with a correct IR spectrum. Fraction (i) was re-separated (col. D; 91°; N_2, 4 l/h) to give ether (2.2 g) and $1H$-undecafluorobicyclo(2,2,1)heptane (0.6 g) with a correct IR spectrum.

Decomposition of lithium undecafluorobicyclo(2,2,1)heptyl (II) in the presence of methyl-lithium

To a well-stirred solution of $1H$-undecafluorobicyclo(2,2,1)heptane (I) (3.0 g) in ether (200 ml) at −55° methyl-lithium (1 *N* from MeBr) was added drop-wise until methane evolution ceased (220 ml). The solution was stirred at −55° for ¼ h and 1 *N* methyl-lithium (from MeBr) (12 ml) added drop-wise and the mixture stirred for ¼ h at −55°. The usual isolation procedure afforded a residue (3.7 g) which was separated by GLC (col. B; 65°; N_2, 14 l/h) to give 4 fractions besides ether. Fraction (i) was a mixture (0.3 g) of 1-methyl-nonafluorobicyclo(2,2,1)hept-2-ene (XXV) (nc) (90 %) and 1-methyl-undecafluorobicyclo-(2,2,1)heptane (XXVI) (10 %) (attempts to separate using other GLC cols. were not successful). Fraction (ii) was 1-bromo-nonafluorobicyclo(2,2,1)hept-2-ene (XXVII) (0.5 g) with a correct IR spectrum[1]. Fraction (iii) was 1,2-dimethyl-octafluorobicyclo(2,2,1)hept-2-ene (XXVIII) (nc) (0.7 g), b.p. 120–121° (Found: C, 40.5; H, 2.2. $C_9H_6F_8$ requires C, 40.6; H, 2.3 %). Fraction (iv) was a mixture of *exo*- and *endo*-1,6-dimethyl-octafluorobicyclo(2,2,1)hept-2-ene (XXIX) (nc) (0.4 g) m.p. 54–56° (sealed tube) (Found: C, 40.1; H, 2.6 %).

The previous experiment was repeated exactly except that *ca.* 2 mole of methyl-lithium (20 ml, 1 *N*) was added to the ethereal solution of the lithio compound at −55°. The usual isolation procedure afforded a residue (4.0 g) which was separated by GLC (col. B; 65°; N_2, 16 l/h) to give: (i) ether; (ii) 1-methyl-nonafluorobicyclo(2,2,1)hept-2-ene (XXV) (0.1 g); (iii) 1,2-dimethyl-octafluorobicyclo(2,2,1)hept-2-ene (XXVIII) (1.0 g); (iv) a mixture of *exo*- and *endo*-1,6-dimethyl-octafluorobicyclo(2,2,1)hept-2-ene (XXIX) (0.3 g); all displayed correct IR spectra.

Characterisation of 1-methyl-nonafluorobicyclo(2,2,1)hept-2-ene (XXV)

The IR spectrum displayed an absorption at 1763 cm^{-1} (–CF=CF–); *m/e* 270 ($C_8H_3F_9$) and a consistent fragmentation pattern; this revealed the presence of a small amount of 1-methyl-undecafluorobicyclo(2,2,1)heptane (XXVI). The ^1H NMR spectrum of a 1 *M* solution in hexafluorobenzene consisted of a singlet at 1.2 (–CH_3).

The olefin (0.1 g) in a stream of nitrogen (10 l/h) over cobaltic fluoride at 80° gave 1-methyl-undecafluorobicyclo(2,2,1)heptane (XXVI) (0.1 g) with a correct IR spectrum[1].

Characterisation of 1,2-dimethyl-octafluorobicyclo(2,2,1)hept-2-ene (XXVIII)

The IR spectrum displayed absorptions at 2920 (CH) and 1710 cm^{-1} (–CF=C(CH_3)–); *m/e* 266 ($C_9H_6F_8$) and a consistent fragmentation pattern. The ^1H NMR spectrum consisted of singlets at 1.6 (–CF=C–CH_3–) and 1.16 (bridgehead CH_3) in the relative intensity ratio of 1:1.

Characterisation of the mixed exo- and endo-1,6-dimethyl-octafluorobicyclo(2,2,1)-hept-2-enes (XXIX)

The IR spectrum displayed an absorption at 1764 (–CF=CF–) with a small absorption at 1718 cm^{-1} attributed to an unidentified impurity; *m/e* 266 ($C_9H_6F_8$)

and a consistent fragmentation pattern. The ^1H NMR spectrum consisted of a doublet (J=25 cps, –CF–CH_3–) one part of which overlapped a singlet (bridgehead CH_3), centred at 1.25 and 1.07, respectively, in the relative intensity ratio of 1:1. The ^{19}F NMR spectrum, which was consistent with the assigned structure, indicated the presence of two isomeric forms.

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