

POLYFLUOROBICYCLO[2.2.2]OCTANES-I 1H-TRIDECAFLUOROBICYCLO[2.2.2]OCTANE, AND SOME DERIVED COMPOUNDS

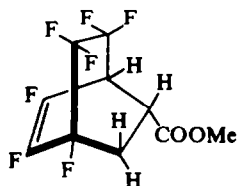
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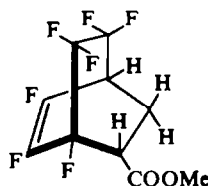
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Abstract—A Diels–Alder reaction between 1H-heptafluorocyclohexa-1,3-diene and methyl acrylate gave two carbomethoxy heptafluorobicyclo[2.2.2]oct-5-enes. Cobaltic fluoride fluorination of each isomer in the vapour phase gave a complex mixture containing tetradecafluorobicyclo[2.2.2]octane (3%), 1H-tridecafluorobicyclo[2.2.2]octane (30%), a mixture of 1H,2H- and 1H,3H-dodecafluorobicyclo[2.2.2]octanes (25%) and a liquid mixture of fragmentation products (40%). The formation of a perfluorocarbanion from 1H-tridecafluorobicyclo[2.2.2]octane has been demonstrated by isotopic exchange in aqueous potassium hydroxide. Lithium tridecafluorobicyclo[2.2.2]octyl has been formed using methyl lithium in ether at -50° and reacted with deuterium oxide, methyl iodide and iodine to give the 1-deutero-, 1-methyl- and 1-iodo-tridecafluorobicyclo[2.2.2]octanes; it was unchanged after 1 hr at 35° and hence represents the most stable perfluoro alkyl lithium so far prepared.

POLYFLUOROBICYCLO[2.2.1]HEPTANES have been prepared by the cobaltic fluoride fluorination of the commercially available hydrocarbon norbornadiene.¹ The properties of the 1H-undecafluorobicyclo[2.2.1]heptane so obtained have prompted us to examine the analogous bicyclo[2.2.2]octane. However, an approach based on the cobaltic fluoride fluorination of bicyclo[2.2.2]oct-2-ene was considered less expedient than a route based on the readily available 1H-heptafluorocyclohexa-1,3-diene (I).² A number of Diels–Alder adducts between octafluorocyclohexa-1,3-diene and various dienophiles, including methylacrylate, have been described.³ We have extended this reaction to the 1H-substituted diene (I) and, using methyl acrylate, prepared two isomeric carbomethoxy heptafluorobicyclo[2.2.2]octenes, viz., 1H-endo-2- and -3-carbomethoxy heptafluorobicyclo[2.2.2]oct-5-ene, (II and III), respectively. No attempt was made to differentiate between these structures. However, cobaltic fluoride fluorination of each isomer gave essentially the same products.

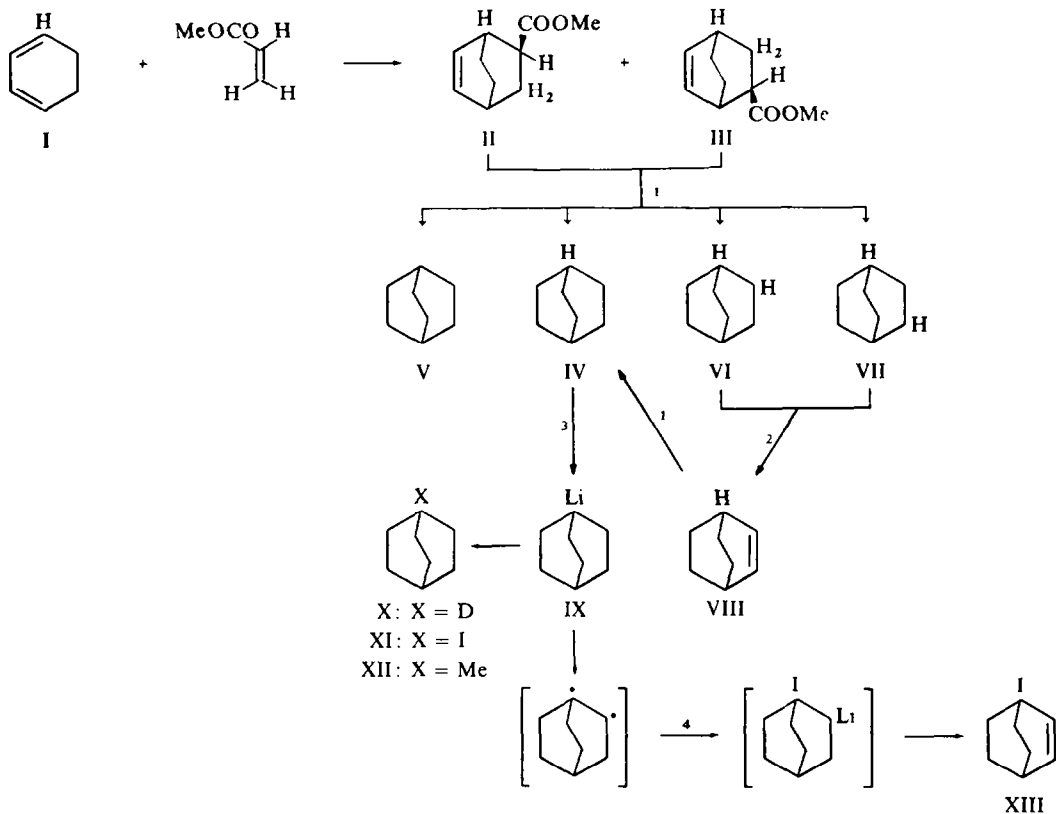


II



III

Cobaltic fluoride has found extensive use in the preparation of saturated polyfluorocarbons.⁴ However, functional groups are usually lost in such fluorinations. In the present work advantage has been taken of this effect to prepare 1H-tridecafluorobicyclo[2.2.2]octane (IV) from the Diels–Alder adducts (II and III). Thus, when



All unmarked bonds are joined to fluorine 1, CoF_3 ; 2, KOHaq ; 3, MeLi ; 4, LiI

fluorinated at 320° in nitrogen as carrier gas, both the solid and the liquid bicyclo[2.2.2]octane isomers (II and III) gave a solid and a liquid product. The former was shown by elemental analysis, IR and ^{19}F NMR spectroscopy and mass spectrometry⁵ to be tetradecafluorobicyclo[2.2.2]octane (V). The liquid portion of the product, which was not examined in detail, was shown by GLC to contain six components and it displayed an IR spectrum typical of a fluorocarbon and closely similar to that of tetradecafluoro methyl cyclohexane; the major component had the same retention time as the latter compound. Parallel fluorinations carried out at 220 – 230° gave a solid and liquid product as before. However, the solid was shown, by the aforementioned techniques, to contain hypodopolyfluorobicyclo[2.2.2]octanes. Hence a larger scale fluorination was completed at 270 – 280° using the mixed solid and liquid Diels–Alder adducts (II and III) and the solid product separated by preparative scale GLC to give tetradecafluoro-, 1 *H*-tridecafluoro- and a mixture of isomeric dihydrododecafluoro-bicyclo[2.2.2]octanes (VI and VII); all were crystalline, high melting, volatile solids.

1*H*-Tridecafluorobicyclo[2.2.2]octane (IV), m.p. 176–178° was characterized by elemental analysis and mass spectrometry.⁵ The IR spectrum of the vapour at 110° revealed a >C—H stretching frequency at 2994.2 cm^{-1} indicating a decreased s-character of this bond as compared with that of the analogous bicyclo[2.2.1]heptane derivative, which displayed a >C—H stretching frequency at 3030.3 cm^{-1} in the vapour state at 20°. The ¹H NMR spectrum consisted of a broad singlet at 6.19 τ consistent with a bridgehead position. The ¹⁹F NMR spectrum was consistent with the proposed structure, in particular it displayed a characteristic multiplet for one bridgehead fluorine.⁶

The third fraction from the GLC separation melted over a seven degree range and was shown by elemental analysis and mass spectrometry⁵ to have the formula C₈H₂F₁₂. The ¹H NMR spectrum displayed two overlapping doublets ($J_{\text{HF}} = 50$ c/s) centred at 4.7 τ , indicating two similarly situated >CHF groups, and a broad singlet at 6.3 τ in the relative intensity ratio of 1:1; this clearly suggests a mixture of the 1*H*,2*H*- and 1*H*,3*H*-dodecafluorobicyclo[2.2.2]octanes (VI and VII), respectively. Confirmation of this allocation of structure was obtained by treatment of the latter mixture with strong aqueous potassium hydroxide at 100°, which gave 1*H*-undecafluorobicyclo[2.2.2]oct-2-ene (VIII) as the sole product and which was in turn fluorinated with cobaltic fluoride at 200° to give 1*H*-tridecafluorobicyclo[2.2.2]octane (IV). The former olefin (VIII) was characterized by elemental analysis, IR and ¹H- and ¹⁹F-NMR spectroscopy. The IR spectrum showed the characteristic absorption of a —CF=CF— group and the ¹H NMR spectrum consisted of a broad singlet centred at 6.02 τ characteristic of a bridgehead proton.

It is well established that polyfluorohydrocarbons with no easy dehydrofluorination pathway available readily undergo deuteration under heterogeneous conditions.¹ In accord with this phenomenon, 1*H*-tridecafluorobicyclo[2.2.2]octane (IV) was 60% deuteriated after 6 hr in a strong solution of potassium hydroxide in deuterium oxide at 100°. Hence, as with the 1*H*-norbornane analogue, the relative stability of the intermediate carbanion derives largely from the inductive field effect of the fluorine substituents and little from negative hyperconjugative stabilization.⁷ It is of added interest to note that the 1*H*-bicyclo octane (IV) still displays such marked acidity even though the s-character of the >C—H bond has diminished compared with the more strained norbornane analogue.

That the 1*H*-bicyclo octane (IV) forms a carbanion under the above conditions was confirmed by its reaction with methyl lithium, prepared from methyl iodide, in diethyl ether at –50°. Methane was rapidly evolved and tridecafluorobicyclo[2.2.1]octyl lithium (IX) formed. This was established by the addition (at –50°) of deuterium oxide which gave 1-deutero-tridecafluorobicyclo[2.2.2]octane (X; 70%) containing 8% of the starting material (IV). Iodine gave 1-iodo-tridecafluorobicyclo[2.2.2]octane (XI; 64%) and methyl iodide gave 1-methyl tridecafluorobicyclo[2.2.2]octane (XII; 60%). The compounds X–XII were characterized by elemental analysis, mass spectrometry, and IR and ¹H- and ¹⁹F-NMR spectroscopy.

The stability of the 1*H*-compound (IV) to strong aqueous alkali at 100° is in agree-

ment with the absence of an easy dehydrofluorination process. Elimination of hydrogen fluoride would be non-planar and the olefin produced would violate Bredt's rule.⁸ However, in marked contrast to undecafluorobicyclo[2.2.1]heptyl lithium, which rapidly eliminates lithium fluoride at about 15° to give a transient bridgehead diradical,¹ tridecafluorobicyclo[2.2.2]octyl lithium (IX) was essentially unaffected after 1 hr at 35°; this was established by hydrolysis to the 1*H*-compound (IV; 82%) and by iodination, which gave the 1-iodo-compound (XI; 32%) together with the 1-methyl-compound (XII; 24%; formed from methyl iodide present in the methyl lithium solution). A trace component was separated which displayed an absorption in its IR spectrum at 1750 cm⁻¹; this might be 1-iodo-undecafluorobicyclo[2.2.2]oct-2-ene (XIII), the anticipated product¹ of decomposition of the lithium compound (IX). Further work on this material is in progress. It is thus clear that the lithium compound (IX) is the most stable perfluoroalkyl lithium so far prepared.

The unexpected difference in ease of elimination of lithium fluoride between tridecafluorobicyclo[2.2.2]octyl lithium (IX) and its norbornyl analogue is clearly not based on stereochemistry, since the bicyclo[2.2.2]octane system (IX) should allow a more nearly coplanar elimination to occur, and the primary decomposition product, the bridgehead "olefin", should be less strained than that from the norbornyl series.

EXPERIMENTAL

Gas chromatography. Analytical work was carried out using glass columns 2 m long × 4 mm diam packed with dinonyl phthalate-kieselguhr (1:2) (Unit A), carbowax-kieselguhr (1:5) (Unit B), Kel-F oil-kieselguhr (1:2) (Unit C), silicone gum-kieselguhr (1:2) (Unit D). For preparative work three copper columns (488 cm × 35 mm) were used. Column A was packed with the same packing as Unit A, column B with that of Unit B and column C with that of Unit D.

NMR spectroscopy. The proton and fluorine spectra were measured with a Varian HA-100 instrument at 94.1 Mc/s, with TMS and CFCl₃ as external references and chemical shifts are quoted in ppm.⁶

Mass spectra. These were measured on an Associated Electrical Industries MS9 instrument.⁵

Diels-Alder reaction of 1H-heptafluorocyclohexa-1,3-diene and methyl acrylate

1*H*-Heptafluorocyclohexa-1:3-diene² (6 × 10.5 g), methyl acrylate (6 × 6 g) and hydroquinone (6 × 0.25 g) were kept at 130° in a sealed "Pyrex" tube for 15 hr. The semi-solid product, after evaporation of any unchanged reactants *in vacuo* (15 mm), was dissolved in hot petrol (b.p. 40–60°; 6 × 100 cc) and cooled to give a crystalline solid (29.2 g); the filtrate was evaporated to a liquid residue (38.4 g). A portion (1.5 g) of the solid was recrystallized from petrol (b.p. 40–60°) to give a *carbomethoxy heptafluoro bicyclo[2.2.2]oct-5-ene* (0.7 g) m.p. 67–69°. (Found: C, 41.2; H, 2.3. C₁₀H₇F₇O₂ requires: C, 41.1; H, 2.4%). A portion (3.0 g) of the liquid product was distilled from phosphoric oxide to give a *carbomethoxy heptafluorobicyclo[2.2.2]oct-5-ene* (3.0 g) b.p. 88°/10 mm. (Found: C, 41.1; H, 2.5%). analytical GLC (Unit D; N₂, 1.5 l./hr; 150°) indicated the presence of one component.

Fluorination of the carbomethoxyheptafluorobicyclo[2.2.2]oct-5-enes

Fluorination procedure. The bicyclo-octenes were passed over a stirred bed of cobaltic fluoride in a standard piece of apparatus⁴ using N₂ as carrier gas. The HF formed during the reaction was removed by passing the products through a tube packed with NaF pellets at 130–150°. The product was collected in a glass trap at –180°.

(a) *The solid isomer.* This compound (6.3 g) was introduced directly into the reactor at 320° during ½ hr in a stream of N₂ (6 l./hr). After a further 1½ hr, the solid product (2.7 g) which deposited near the inlet of the trap was separated from the liquid product (1.2 g) and sublimed (65°/17 mm) from phosphoric oxide to give *tetradecafluorobicyclo[2.2.2]octane* (1.5 g) m.p. 184–186° (sealed tube). (Found: C, 26.7; F, 72.9. C₈F₁₄ requires: C, 26.5; F, 73.5%) which was shown by GLC analysis (Unit B; N₂, 1.3 l./hr; 100°) of a solution in hexafluorobenzene to contain one component. Mass spectrometry gave a top mass peak of 363 (C₈F₁₄) and a consistent fragmentation pattern,⁵ the ¹⁹F NMR spectrum of a 0.5M solution in hexafluorobenzene consisted of a doublet (*J* = 6.9 c/s) at 124.1 and a broad band centred at 220.3 in the relative

intensity ratio of 6:1. The IR spectrum of the vapour consisted of four absorptions with maxima at 1300, 1250, 1000 and 960 cm^{-1} .

The liquid part (1.2 g) of the fluorination product was shown by GLC (Unit C; N_2 , 1.0 l./hr; 42°) to contain 6 components; the principal component displayed the same retention time as tetradecafluoromethyl cyclohexane and the IR spectrum of the mixture was very similar to that of the latter compound.

(b) *The liquid isomer.* This compound (1.2 g) was subjected to exactly the same procedure (320°) to give a solid (0.45 g) and a liquid (0.3 g) in the product trap. The solid was shown by IR spectroscopy and GLC (Unit A; N_2 , 1.3 l./hr; 100°) to contain only tetradecafluorobicyclo[2.2.2]octane. The liquid product was shown by GLC (Unit C; N_2 , 1.0 l./hr; 42°) to be a complex mixture.

(c) *The solid isomer.* This Diels Alder adduct (7.2 g) was also fluorinated in the standard manner at 220–230° to give a solid (3.2 g) and a liquid (0.9 g) in the product trap. A portion (1.5 g) of the solid was sublimed (90–120°/10 mm) and the sublimate was shown by GLC (Unit A; N_2 , 1.0 l./hr; 76°) of a soln in perfluoromethylcyclohexane to be a mixture of tetradecafluorobicyclo[2.2.2]octane and 1*H*-tridecafluorobicyclo[2.2.2]octane with relative peak areas of ca. 1:3, respectively.

(d) *The liquid isomer.* This Diels–Alder adduct (0.9 g) was similarly fluorinated at 270–280° to give a solid (0.5 g) and a liquid (0.2 g) in the product trap. The solid was sublimed and shown by GLC (Unit A; N_2 , 1.0 l./hr; 76°) to contain tetradecafluorobicyclo[2.2.2]octane and 1*H*-tridecafluorobicyclo[2.2.2]octane.

Examination of the solid product formed in a series of cobaltic fluoride fluorinations of the solid and liquid Diels–Alder adducts at 270–280°

The total solid product (35.0 g) was sublimed (120°) to give a white crystalline solid (28 g) which was shown by GLC (Unit B; N_2 , 1.0 l./hr; 100°) to contain 3 components in addition to the solvent (hexafluorobenzene). A portion (24.0 g) of the latter solid was separated by preparative GLC (column B; N_2 , 14 l./hr; 100°) to give:

(i) tetradecafluorobicyclo[2.2.2]octane containing 1*H*-tridecafluorobicyclo[2.2.2]octane (<20% by GLC; 0.8 g);

(ii) 1*H*-tridecafluorobicyclo[2.2.2]octane (5.9 g) m.p. 176–178° (sealed tube). (Found: C, 27.7; H, 0.2; F, 71.6. C_8HF_{13} requires: C, 27.9; H, 0.3; F, 71.8%), γ_{max} 2994.2 cm^{-1} (>CH) (in vapour state at 110°), the ^1H NMR of a saturated solution in CFCl_3 consisted of a broad singlet centred at 3.8, the ^{19}F NMR spectrum of a 1M soln in hexafluorobenzene consisted of a single band at 110, a doublet at 121.6 and a complex multiplet at 221.3 in the relative intensity ratio of 6:6:1, mass spectrometry gave a top mass peak at 344 (C_8HF_{13});

(iii) a mixture of isomeric dihydrododecafluorobicyclo[2.2.2]octanes (5.3 g) m.p. 167–174° (sealed tube). (Found: C, 29.5; H, 0.7; F, 70.9. $\text{C}_8\text{H}_2\text{F}_{12}$ requires: C, 29.4; H, 0.6; F, 69.9%), mass spectrometry gave a top mass peak at 326 ($\text{C}_8\text{H}_2\text{F}_{12}$), the ^1H NMR spectrum of a saturated soln in CFCl_3 consisted of two overlapping doublets ($J = 50$ c/s) centred at 5.3 (>CHF) and a broad singlet centred at 3.7 in the total relative intensity ratio of 1:1 (suggesting a mixture of the 1*H*:2*H*- and 1*H*:3*H*-isomers).

The above dihydro-dodecafluorobicyclo[2.2.2]octanes (2×1.9 g) and 50% KOH aq (2×25 cc) were shaken together in a sealed tube at 100° for 24 hr and then extracted with ether. The dried (MgSO_4) ether soln was filtered and fractionated to leave a liquid residue (4.1 g) which was separated by preparative scale GLC (column A; N_2 , 15 l./hr; 85°) to give: (i) ether (1.1 g); (ii) crystalline 1*H*-undecafluorobicyclo[2.2.2]oct-2-ene (0.5 g). (Found: C, 31.3; H, 0.1. C_8HF_{11} requires: C, 31.4; H, 0.3%), γ_{max} 1760 cm^{-1} (—CF=CF—), the ^1H NMR spectrum of a soln in CDCl_3 consisted of a broad singlet centred at 3.9, the ^{19}F NMR spectrum of a soln in CDCl_3 consisted of two AB spectra centred at 112 and 124, a doublet ($J = 13$ c/s) centred at 136, a singlet at 148.6 and a singlet at 224 (CCl_3F as internal standard) in the relative intensity ratio of 4:4:1:1:1.

The above olefin (0.2 g) was passed in a stream of N_2 over a stirred bed of cobaltic fluoride (150 g) at 200° to give 1*H*-tridecafluorobicyclo[2.2.2]octane (0.2 g) with a correct IR spectrum.

1-Iodo-tridecafluorobicyclo[2.2.2]octane

1*H*-Tridecafluorobicyclo[2.2.2]octane (1.0 g) in dry Na–ether (50 cc) was stirred at -78° and an ethereal soln of MeLi (0.8N, from MeI) was added dropwise until CH_4 evolution ceased (ca. 70 cc). The soln was stirred at -78° for $\frac{1}{2}$ hr and I_2 (1.0 g) in ether (20 cc) was added; this mixture was stirred for 2 hr at room temp and then shaken with $\text{Na}_2\text{S}_2\text{O}_3$ aq. The I_2 -free ether soln was dried (MgSO_4) and evaporated *in vacuo*

to a brown residue (1.0 g) which was distilled from P_2O_5 to give 1-iodotridecafluorobicyclo[2.2.2]octane (0.9 g) m.p. 108–111° (sealed tube). (Found: C, 20.3; H, 0.0; F, 53.2. $C_8F_{13}I$ requires: C, 20.4; F, 52.5%), mass spectrometry gave a top mass peak at 470 ($C_8F_{13}I$), the ^{19}F NMR spectrum of a soln in $CDCl_3$ consisted of a doublet ($J = 3.3$ c/s) centred at 107, a doublet ($J = 10.3$ c/s) centred at 127 and a broad band at 223 in the relative intensity ratio of 6:6:1.

Deuteration of tridecafluorobicyclo[2.2.2]octyl lithium

1H-Tridecafluorobicyclo[2.2.2]octane (1.0 g) was converted to tridecafluorobicyclo[2.2.2]octyl lithium in the manner described previously and, after stirring at 0° for $\frac{1}{2}$ hr, D_2O (10 g) was added at 0° and the stirring continued for 1 hr at 18°. The ether layer was then separated, dried ($MgSO_4$), filtered and evaporated to give a solid which was sublimed to give a tridecafluorobicyclo[2.2.2]octane (0.7 g) which was shown by mass spectrometry to contain 92% deuterium.

Partial deuteration of 1H-tridecafluorobicyclo[2.2.2]octane.

This compound (0.5 g), D_2O (15 g) and KOH (10 g) were shaken together in a sealed tube at 100° for 6 hr. The tube was then opened and the solid (0.5 g), filtered and sublimed from P_2O_5 to give a tridecafluorobicyclo[2.2.2]octane (0.4 g) which was shown by mass spectrometry to contain 60% deuterium.

The stability of tridecafluorobicyclo[2.2.2]octyl lithium in diethyl ether

A 0.4N soln of MeLi in ether was added to a stirred solution of 1H-tridecafluorobicyclo[2.2.2]octane (2.3 g) in ether (150 cc) until CH_4 evolution (180 cc) ceased. The resulting colourless soln was stirred for $\frac{1}{2}$ hr at -78° , for $\frac{1}{2}$ hr at 18° and finally for 1 hr at 35°. The ether soln, which contained only a small amount of ppt, was then shaken with dilute acid and then with water and dried ($MgSO_4$), filtered and evaporated. The liquid residue (5 cc) was shown by GLC (Unit A; N_2 , 1.0 l./hr; 100° and Unit D; N_2 , 1.3 l./hr; 100°) to contain two peaks with retention times identical to those of 1H-tridecafluorobicyclo[2.2.2]octane and diethyl ether. The solvent was then removed *in vacuo* and the solid (1.9 g) sublimed to give 1H-tridecafluorobicyclo[2.2.2]octane (1.6 g) with a correct IR spectrum.

1H-Tridecafluorobicyclo[2.2.2]octane (2.0 g) was treated with ca. 0.1N MeLi in precisely the manner described above to give methane (130 cc), and after 1 hr at 35° a soln of I_2 (1.5 g in ether 10 cc) was added (there was a rapid decolourization until the last few drops were added) and the mixture kept at 35° for 1 hr. The ether layer was then washed with $Na_2S_2O_3$ aq, washed with water, dried ($MgSO_4$), filtered and distilled. The residue (4.5 g) so obtained was shown by GLC (Unit D; N_2 , 1.0 l./hr; 110°) to be free from starting material and to contain 3 components in addition to ether which were separated by GLC (column C; N_2 , 1.5 l./hr; 100°) to give (i) ether (2.0 g); (ii) 1-methyl tridecafluorobicyclo[2.2.2]octane (0.5 g) m.p. 185–186° (sealed tube). (Found: C, 30.2; H, 0.8; F, 69.0. $C_9H_3F_{13}$ requires: C, 30.2; H, 0.8; F, 69.0%), mass spectrometry gave a top mass peak at 358 ($C_9H_3F_{13}$), the 1H NMR spectrum of a soln in $CDCl_3$ consisted of a singlet at 3.6 (TMS as internal standard), the ^{19}F NMR spectrum consisted of a singlet at 118 a doublet ($J = 10.3$ c/s) centred at 122 and a band at 223 in the relative intensity ratio of 6:6:1; (iii) an unsaturated polyfluorocarbon (trace amount) γ_{max} 1750 and 1680 cm^{-1} ; (iv) 1-iodotridecafluorobicyclo[2.2.2]octane (0.9 g) m.p. 108–111° (sealed tube) with a correct IR spectrum.

1-Methyl-tridecafluorobicyclo[2.2.2]octane

1H-Tridecafluorobicyclo[2.2.2]octane (1.0 g) in dry ether (50 cc) was stirred at 0° and an ethereal soln of MeLi (0.8N, from MeI) was added dropwise until CH_4 evolution ceased (70 cc). MeI (3.0 g) was then added and the mixture refluxed for 24 hr, washed with water and the ether layer dried ($MgSO_4$), filtered and evaporated. The residue (0.75 g) was shown by analytical GLC (Unit A; N_2 , 1.0 l./hr; 100°) to contain ether, MeI and one other component of shorter retention time than starting material. After removal of the last traces of ether and MeI the solid residue was sublimed to give 1-methyl-tridecafluorobicyclo[2.2.2]octane (0.6 g), m.p. 185–186° (sealed tube) with a correct IR spectrum.

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