Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

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

R. STEPHENS, J. C. TATLOW AND K. N. WOOD
Chemistry Department, The University, P.O. Box 363, Birmingham B15 2TT (Great Britain)

(Received April 16th, 1971)

SUMMARY

1*H*,4-Methyl-decafluorobicyclo(2,2,1)heptane made from the 1*H*,4*H* analogue was fluorinated by cobaltic fluoride to the title compound, which after lithiation was converted to the derivatives (1)$CF_3 \cdot C_7F_{10} \cdot X$(4); X = D, I, Br, CH_3, CO_2H. Decomposition of the relatively stable 1-lithio derivative in refluxing ether went via a transient bridgehead olefin to give 1-iodo-4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene or a related species depending on the lithium derivative present in the system. Most derivatives of the type (1)$X \cdot C_7F_{11}$ and (1)$X \cdot C_7F_{10} \cdot X$(4) are solids.

INTRODUCTION

Work[1,2] on polyfluorobicyclo(2,2,1)heptane derivatives with substituents on positions 1 and 4 has shown that the two bridgehead positions can exert considerable influence on each other. The synthesis[1] of 1*H*,4-methyl-decafluorobicyclo(2,2,1)heptane (I) afforded a precursor from which trifluoromethyl-substituted compounds might be made. The influence of the $-CF_3$ group in this field was of interest.

RESULTS AND DISCUSSION

The most convenient method of preparation of the 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) involved the cobaltic fluoride fluorination of the 1*H*,4-methyl analogue (I) obtained[1] from 1-lithio-4,*H*-decafluorobicyclo-(2,2,1)heptane and methyl iodide. Difficulties were encountered, however, in the

---

* For Part III, see ref. 1.

large-scale GLC separation of the 1*H*,4-methyl- (I) and the simultaneously-formed 1,4-dimethyl-decafluorobicyclo(2,2,1)heptane (III), but were surmounted by fluorination of an incompletely separated fraction containing (I) and (III) in the ratio of 9:1. Preliminary work revealed that the 1,4-dimethyl compound (III) was almost completely converted to 1,4-bis-trifluoromethyl-decafluorobicyclo-(2,2,1)heptane (IV) at temperatures below that required to fluorinate the bridgehead hydrogen in 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II). Fluorination of the 1,4-dimethyl compound (III) gave increasing amounts of the perfluorocarbon (IV) over the temperature range 180–290°. The conversion[3] of methyl- to trifluoromethyl-undecafluorocyclohexane by cobaltic fluoride occurs without accompanying intermediates, and the present fluorination was unusual in that an intermediate, 1-difluoromethyl-4-trifluoromethyl-decafluorobicyclo-(2,2,1)heptane (V) could be isolated in substantial amounts (53% at 180°).

The 1:9 mixture of the 1,4-dimethyl (III) and 1*H*,4-methyl (I) compounds was fluorinated over cobaltic fluoride at 300°, and perfluorocarbon compounds removed by azeotropic distillation with acetylacetone. The residue afforded 1-difluoromethyl-4-trifluoromethyl- (V) and, as the principal product, 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II).

1*H*,4-Trifluoromethyl-decafluorobicyclo(2,2,1)heptane displayed a high C–H stretching frequency (3030 cm^{-1}) and a singlet at 6.5 τ in its ^1H NMR spectrum characteristic[4] of the bridgehead position of polyfluorobicyclo(2,2,1)heptanes; it is likely that the compression of bond angles at C_1 results in an increased s character for this bond. The ^{19}F NMR spectrum, also typical of perfluorobicyclo-(2,2,1)heptane derivatives, is described in Figure 1 and displayed the anticipated relative intensity ratios.

As with 1*H*-undecafluoro- and 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane[4] and 1*H*-tridecafluorobicyclo(2,2,2)octane[5], 1*H*,4-trifluoromethyl-decafluorobicyclo-(2,2,1)heptane (II) was quantitatively recovered after treatment with strong aqueous potassium hydroxide at 100°, but underwent extensive deuteriation (75.5%) when treated with potassium hydroxide in deuterium oxide. The higher degree of deuteriation (81.7%) of 1*H*-undecafluorobicyclo(2,2,1)heptane under identical conditions does not necessarily imply a higher degree of acidity for the latter, since solubility differences may be vital under the heterogeneous conditions employed. For example, 1*H*-tridecafluorobicyclo(2,2,2)octane incorporates less deuterium (78%) than the bicyclo(2,2,1)heptyl analogue (80%) under identical heterogeneous conditions, but is known to undergo isotopic exchange in a homogeneous system with sodium methoxide in tritiated methanol 100-times faster than 1*H*-undecafluorobicyclo(2,2,1)heptane[6].

Formation of a carbanionic species by 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) in aqueous alkali was confirmed by the evolution of 1 mol. of methane when it was treated with methyl-lithium in ether at −60°. The derived organo-lithium (VI) was trapped at −60° with iodine, bromine, methyl iodide and carbon dioxide to give 1-iodo- (VII) (76%), 1-methyl- (VIII) (64%) and 1-bromo- (IX) (71%) -4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane, and 4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane-1-carboxylic acid (X) (80%), respectively.

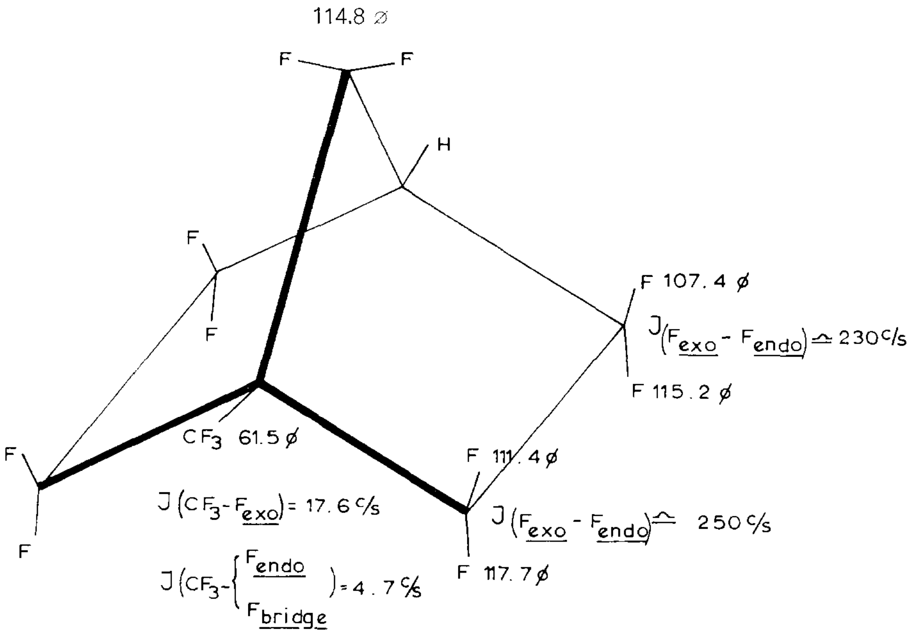


Fig. 1. ^{19}F NMR absorption and coupling frequencies.

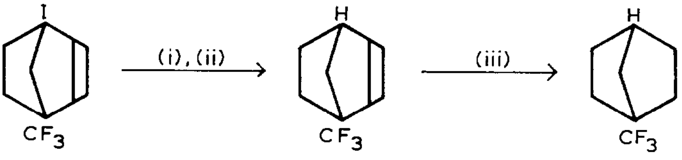
1-Iodo- (VII) and 1-bromo-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (IX) were both readily reduced with lithium aluminium hydride (LAH) to the 1*H*-4-trifluoromethyl compound (II) (82% and 77%, respectively), in agreement with the behaviour of the bridgehead halides described earlier[1,2].

1-Methyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VIII) was fluorinated with cobaltic fluoride to give 1,4-bis-trifluoromethyl-decafluorobicyclo-(2,2,1)heptane (IV) (58%).

Like the other polyfluoro bridgehead carboxylic acids, the 4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane-1-carboxylic acid (X) appeared to decarboxylate on melting, but was not particularly unstable. The acid was methylated with diazomethane, and the methyl ester produced was reduced with LAH to the known[7] 4-trifluoromethyl-decafluorobicyclo(2,2,1)hept-1-yl methanol.

The presence of the bridgehead trifluoromethyl group appeared to have a stabilizing effect on the organo-lithium compound (VI). Thus, appreciable decomposition of an ethereal solution of (VI), prepared from the 1*H* compound (II) and 1.2 mol. of methyl-lithium (from MeI), appeared to occur only under reflux. The principal products (see Figure 3) were 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II), 1-iodo-4-trifluoromethyl-octafluorobicyclo(2,2,1)-hept-2-ene (XI) (the major one), and 1-iodo-4-trifluoromethyl-decafluorobicyclo-(2,2,1)heptane (VII). The last compound was identical with that obtained from the lithio compound (VI) and iodine. 1*H*,4-Trifluoromethyl-octafluorobicyclo-(2,2,1)hept-2-ene (XII), 1-methyl-4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XIII), and 1-methyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VIII) were obtained as an admixture of minor products and were identified by IR spectroscopy.

The hitherto unknown principal product (XI) was identified by IR and NMR spectroscopy and mass spectrometry, and unequivocally related to 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) by the sequence depicted in Figure 2.



(XI) (XII) (II)

(i) Mg ; (ii) 4N HCl ; (iii) CoF_3

Fig. 2. Characterization of the 1*H*,4-CF_3-bicyclo-ene (XI).
(All unmarked substituents are fluorine.)

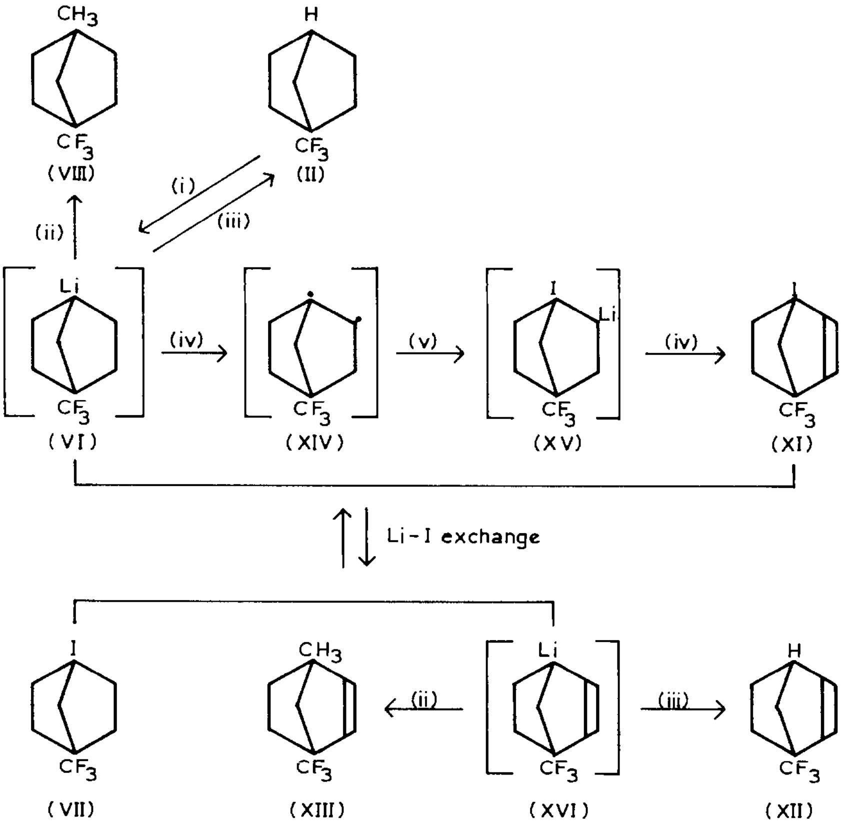
The Grignard reagent involved in Figure 2, like those derived from 2-enes described previously, displayed a high stability in refluxing ether.

The decomposition products can readily be explained by a pathway related to those invoked before[1,2,4]. Thus, as set out in Figure 3, the 1-lithio-4-trifluoromethyl compound (VI) loses lithium fluoride to give the bridgehead olefin or diradical (XIV) which adds lithium iodide (methyl-lithium derived from methyl iodide) to give (XV) which in turn gives, by loss of lithium fluoride, the iodo olefin (XI). The latter olefin (XI) and the 1-lithio compound (VI) then undergo a lithium–iodine exchange reaction, and enter into equilibrium with the saturated iodide (VII) and the unsaturated lithio compound (XVI). The latter should be stable under the reaction conditions and would then be protonated during the isolation procedure to give (XII).

The products (XIII) and (VIII) arise from the reaction of small amounts of methyl iodide [residual from the methyl-lithium used to generate the 1-lithio compound (VI)] with lithio compounds (XVI) and (VI), respectively.

The comparable decomposition of 1-lithio-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VI) generated from the 1*H*-fluorocarbon (II) and 1.3 mol.

of methyl-lithium derived from methyl bromide gave 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) and 1-bromo-4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XVII) as the principal products, and trace amounts of 1*H*,4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XII) and 1-bromo-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (IX). The latter was shown to be present as trace amounts in admixture with the bromo olefin (XVII) by mass spectrometry.



(i) CH_3Li ; (ii) CH_3I ; (iii) 4N HCl ; (iv) loss of LiF ; (v) LiI

Fig. 3. Decomposition of lithiated 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane(VI). (All unmarked substituents are fluorine; species in brackets were not isolated.)

1-Bromo-4-trifluoromethyl-octafluorobicylo(2,2,1)hept-2-ene (XVII) was identified by IR spectroscopy and mass spectrometry, and by its cobaltic fluoride fluorination to 1-bromo-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (IX) (75%).

The products so obtained are clearly derived in a similar pathway to that depicted in Figure 3. Thus, the lithium compound (VI) loses lithium fluoride to give the diradical (XIV) and this adds lithium bromide to give the bromo analogue of (XV) which loses lithium fluoride to give (XVII), the bromo analogue of the olefin (XI).

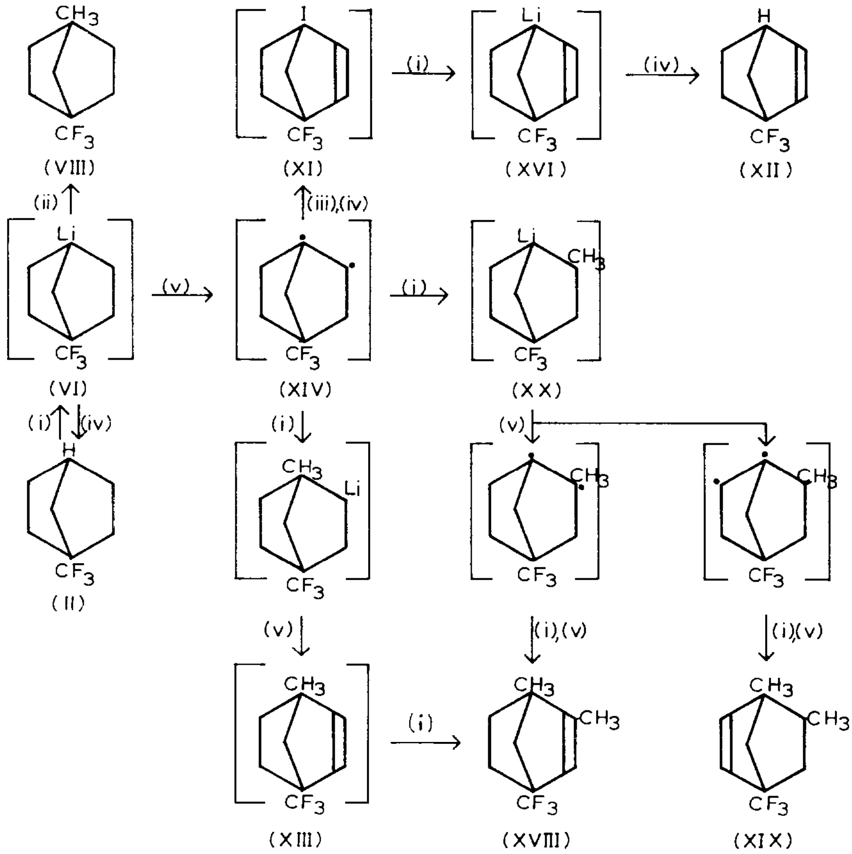
The smaller total recovery of volatile material compared with that from the former decomposition (Fig. 3) might result from the lower solubility of lithium bromide in ether which permits alternative reactions (such as dimerization) of the diradical to less volatile products. A similar difference exists between the total recovery of volatile materials in the analogous decompositions[4] of 1-lithio-undecafluorobicyclo(2,2,1)heptane, and would arise in the same way. The trace amount of 1-bromo-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (IX) isolated would be compatible with a less-favourable bromine–lithium exchange[1] between the bromo olefin (XVII) and the 1-lithio compound (VI).

Since more than 1 mol. of methyl-lithium was used in both decomposition reactions, the substantial amounts of 1*H*,4-trifluoromethyl-decafluorobicyclo-(2,2,1)heptane (II) isolated must arise from hydrolysis of the 1-lithio-4-trifluoromethyl compound (VI) during the isolation procedure. This lithio compound, having survived 2 h at 35°, must accordingly be more stable than 1-lithio-undecafluorobicyclo(2,2,1)heptane[4] and 1-lithio-4,*H*-decafluorobicyclo(2,2,1)heptane[1], which are completely decomposed by these conditions.

When an excess of methyl-lithium (*ca.* 2.5 mol.) was used in the generation and subsequent decomposition of 1-lithio-4-trifluoromethyl-decafluorobicyclo-(2,2,1)heptane (VI), the products formed from the transient bridgehead olefin (XIV) arose via the powerful nucleophile methyl-lithium, but were also dependent on the presence of lithium iodide or lithium bromide. Thus, after 1 h reflux, 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VI) and 2.5 mol. of methyl-lithium, derived from methyl iodide, in ether gave 1-methyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VIII) (7%), 1*H*,4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XII) (26%), a trace amount of 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) and an inseparable mixture of 1,2-, 1,6-*exo*- and 1,6-*endo*-dimethyl-4-trifluoromethyl-heptafluorobicyclo(2,2,1)hept-2-ene ((XVIII) and (XIX)) (39%). The ratio of 1,2- to 1,6-dimethyl isomers was established by ^{19}F NMR spectroscopy as 4:1, respectively. However, the same process using 2.6 mol. of methyl-lithium derived from methyl bromide gave the same inseparable mixture of 1,2- and 1,6-dimethyl olefins ((XVIII) and (XIX)) (60%) in the ratio of 17:3, respectively, but only trace amounts of the other three components obtained in the presence of lithium iodide.

1*H*,4-Trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XII) was characterized by analysis, IR and ^{1}H and ^{19}F NMR spectroscopy and mass spectrometry, and by cobaltic fluoride fluorination to 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II).

The major product from both decompositions, a mixture of isomeric olefins, was shown by elemental analysis and mass spectrometry to have the molecular formula $C_{10}H_6F_{10}$. Mass spectrometry also gave fragments of *m/e* 216, 220 and 96 which can be allocated to the molecule ions arising in a retro-Diels–Alder mechanism, *viz.*, 1,2-dimethyl-4-trifluoromethyl-trifluorocyclopenta-1,3-dienyl cation ($C_8H_6F_6^+$), the 1-methyl-4-trifluoromethyl-tetrafluorocyclopenta-1,3-dienyl cation ($C_7H_3F_7^+$) and the methyl trifluoroethylene cation ($C_3H_3F_3^+$); their relative abundancies were consistent with a predominance of the 1,2-dimethyl isomer, as were also the relative intensities of the double-bond stretching frequencies in the IR spectrum. The ^1H and ^{19}F NMR spectra were consistent with the assigned structures, and indicated the proportions of the two isomers; *viz.*, 4:1 (LiI present) and 17:3 (LiBr present). The reaction scheme for these processes is set out in Figure 4. It could be that addition of methyl-lithium to the bridgehead diradical



(i) CH_3Li ; (ii) CH_3I ; (iii) LiI ; (iv) 4N HCl ; (v) loss of LiF

Fig. 4. Decomposition of the lithiate (VI) in the presence of methyl-lithium.
(All unmarked substituents are fluorine; species in brackets were not isolated.)

(XIV) is unidirectional to give (XX). However, it may also be that the olefin (XIII) which would be obtained via the reverse addition undergoes rapid addition–elimination to give (XVIII), and does not survive to be isolated (unlike the 4*F* analogue[2]). When lithium iodide is present, a competing addition to (XIV) leads to 1-iodo-4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XI) (lithium bromide is much less effective in this respect). Again this is not found, but it should readily undergo halogen–metal exchange with methyl-lithium to give the 1-lithio-4-trifluoromethyl olefin (XVI). Substitution products of the 1*H*-trifluoromethyl olefin (XII) were not found, presumably because this olefin (XII) will exist as its strongly deactivated lithio derivative (XVI) until the addition of mineral acid.

The mixed dimethyl olefins should arise as depicted in Figure 4. Although the origin of all of the 1,2-dimethyl isomer (XVIII) isolated is obscured by the possible intermediary of the olefin (XIII), the detection of a 1,6-dimethyl olefin (XIX) is unequivocal evidence for nucleophilic attack at C_2 of the diradical (XIV), as was the case[2] for the 4-fluoro-substituted diradical described earlier. It is noteworthy that again a little of the original lithiate (VI) appeared to survive, since (II) was found.

Though it is too early to generalize, it appears that the strongly electron-attracting $-CF_3$ group, when in position 4 of a decafluorobicyclo(2,2,1)heptane system, does not have the same influence on position 1 as a fluorine. The stabilizing effect on organo-metallics seems to be $CF_3 > H > F$.

The work in this paper, like the earlier ones, has clearly shown the many synthetic opportunities available in this series, and has given many new products with potentially valuable properties. It is of interest to note that most derivatives of the type $(1)X.C_7F_{11}$ and $(1)X.C_7F_{10}.X'(4)$ prepared in work described in this paper, and earlier parts of the series, are solids, some of them quite volatile. The 2-ene analogues usually have lower melting points.

EXPERIMENTAL

Gas chromatography, spectroscopy, etc. were as described[2] in Part II.

Preparative

1H-4-*Methyl-* (I) *and* 1,4-*dimethyl-decafluorobicyclo*(2,2,1)*heptane* (III)

A larger-scale reaction than that described[1] utilized the 1*H*,4*H*-decafluoride (250 g), methyl-lithium (22.0 g, from MeBr) and then methyl iodide (134 g). GLC separation of the product (Col. J; 85°; N_2 70 l/h) gave (III) (60 g), a 9:1 mixture of (I) and (III) (105 g) and the 1*H*,4*H*-decafluoride (43 g).

Fluorination of 1,4-*dimethyl-decafluorobicyclo*(2,2,1)*heptane* (III)

The title compound (in N_2, 3 l/h) was passed over CoF_3 at the various temperatures set out in Table 1. The solid product was dissolved in diethyl ketone

TABLE I

Temp. (°C)	CH_3–C_7F_{10}–CH_3 (g)	CF_3–C_7F_{10}–CF_3 (g)	% yield	CF_3–C_7F_{10}–CF_2H (g)	% yield	Other Products (g)
180	3.2	0.5	12	2.2	53	0.8
200	4.0	1.2	24	2.0	39	0.8
250	1.8	0.7	28	0.8	34	0.2
290	0.5		95*		5*	

* Estimated by comparison of analytical GLC peak areas.

and separated by GLC (col. A; 60°; N_2, 15 l/h) to give, besides solvent, (i) 1,4-bis-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (IV) (nc), b.p. 109–110°, (Found: C, 26.2. C_9F_{12} requires C, 26.2%), *m/e* 412 (vw) (C_9F_{16}), 393 (intense) (C_9F_{15}); (ii) 1-difluoromethyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (V) (nc), m.p. 29° (sealed tube), b.p. 123–124° (Found C, 27.4; H, 0.4. C_9HF_{15} requires C, 27.4; H, 0.3%), $\nu_{max.}$ 3008 cm^{-1} (vw) (CH), *m/e* 374 (C_9F_{14}), 51 (CF_2H), its ^1H NMR spectrum consisted of a triplet (*J*(HF) 52.5 cps) centred at 3.6 τ; (iii) mixtures of 5–7 components which were not investigated further.

1H-*Trifluoromethyl-decafluorobicyclo*(2,2,1)*heptane* (II)

A mixture (21.0 g) of 1,4-dimethyl- (III) (10%) and 1*H*-4-methyl-decafluoro-bicyclo(2,2,1)heptane (I) (90%) (in N_2, 2.5 l/h) was passed over CoF_3 at 300°. A solution in acetyl acetone of a portion of the solid product from five such fluorinations was shown by GLC (col. K; 80°; N_2, 4.5 l/h) to contain one major product. The minor perfluorocarbons were removed by azeotropic distillation (vacuum-jacketed column, 35 cm × 2.5 cm packed with glass helices) and shown by GLC (col. K; 50°; N_2, 4.5 l/h) to be mainly 1,4-bis-trifluoromethyl-decafluoro-bicyclo(2,2,1)heptane (IV) with a correct IR spectrum. The components of the residue were separated by GLC (col. J; 85°; N_2, 60 l/h) to give, besides acetyl-acetone, three fractions. Fraction (i) was 1-difluoromethyl-4-trifluoromethyl-deca-fluorobicyclo(2,2,1)heptane (V) (2.8 g) with a correct IR spectrum. Fraction (ii) was 1*H*-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (nc) (69.5 g) m.p. 105–106° (sealed tube) (Found: C, 27.8; H, 0.5. C_8HF_{13} requires C, 27.9; H, 0.3%), $\nu_{max.}$ 3030 cm^{-1} (w) (bridgehead H), *m/e* 344 (w) (C_8HF_{13}), 325 (i) (C_8HF_{12}); its ^1H NMR spectrum consisted of a broad absorption at 6.5 τ (bridgehead H). Fraction (iii) was a mixture (3.0 g) which was separated (col. A; 80°; N_2, 18 l/h) to give (a) 1,4-dimethyl-decafluorobicyclo(2,2,1)heptane (III) (0.2 g) with a correct IR spectrum, (b) 1*H*-4-methyl-decafluorobicyclo(2,2,1)heptane (I) (1.4 g) with a correct IR spectrum, and (c) a mixture (trace amount) of three components whose IR spectrum displayed $\geqslant$CH stretching frequencies around 2980 cm^{-1}, and absorptions characteristic of a highly-fluorinated bicyclo(2,2,1)heptane system.

Partial deuteriation of 1H,4-*trifluoromethyl-decafluorobicyclo*(2,2,1)*heptane*(II)

This compound (0.3 g), KOH (1.0 g) and D_2O (1.0 g) were shaken together in a sealed tube for 3 h at 100°. The tube was then opened, the organic layer dried (P_2O_5) and distilled *in vacuo* to give a solid (0.3 g) with an IR spectrum different from that of the starting material but transparent in the range 1700–2000 cm^{-1} (saturated fluorocarbon). Mass spectrometry revealed C_8DF_{13} (75.5%) and C_8HF_{13} (24.5%).

A control using 1*H*-undecafluorobicyclo(2,2,1)heptane gave C_7DF_{11} (81.7%) and C_7HF_{11} (18.3%).

1-*Iodo*-4-*trifluoromethyl-decafluorobicyclo*(2,2,1)*heptane* (VII)

1*H*-4-Trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (2.5 g) and methyl-lithium (1.2 *N*, from MeI) in ether were mixed as before at −60° (150 ml CH_4 evolved), iodine (2.4 g) in ether (25 ml) added, and the solution allowed to attain room temperature. The ether layer was treated in the usual way, and the residue separated by GLC (col. B; 80°; N_2, 18 l/h) to give, besides ether, 1-iodo-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VII) (nc) (2.6 g) m.p. 32–34° (Found: C, 20.5; I, 26.5. $C_8F_{13}I$ requires C, 20.4; I, 27.0%), *m/e* 470 ($C_8F_{13}I$).

LAH (0.5 g) in dry ether (20 ml) was added slowly to a stirred solution of the iodide (VI) (0.5 g) in dry ether (50 ml) at 0°. The solution was refluxed for 30 min and stirred for 12 h at room temperature, then cooled to 0°, water (10 ml) slowly added followed by 4 *N* HCl (30 ml). The ethereal layer gave, in the usual way, a residue which was separated by GLC (col. N; 70°; N_2, 3.5 l/h) to give, besides ether, 1*H*-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (0.3 g) with a correct IR spectrum.

1-*Methyl*-4-*trifluoromethyl-decafluorobicyclo*(2,2,1)*heptane* (VIII)

1*H*-4-Trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (2.1 g) and methyl-lithium (1.5 *N* from MeBr) in ether were mixed as usual, methyl iodide (10 g) added, and the stirring continued for a further hour. The solution was then allowed to attain room temperature, 4 *N* HCl (15 ml) added, the ethereal layer treated in the usual way to give a residue which was separated by GLC (col. N; 60°; N_2, 3.5 l/h) to give, besides ether and a trace of methyl iodide, 1-methyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VIII) (nc) (1.4 g) m.p. 73–74° (Found: C, 30.5; H, 0.9. $C_9H_3F_{13}$ requires C, 30.2; H, 0.8%), $\nu_{max.}$ 2950 cm^{-1} (CH_3), *m/e* 343 (s) (C_8F_{13}), 339 (s) ($C_9H_3F_{12}$), 158 ($C_5H_3F_5$), 127 ($C_4H_3F_4$), 69 (CF_3) and 15 (CH_3); its ^1H NMR spectrum consisted of a broad singlet at 8.5 τ.

1-Methyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VIII) (0.3 g) was passed in N_2 (3 l/h) over CoF_3 at 300° to give 1,4-bis-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (IV) (0.2 g) with a correct IR spectrum and GLC retention volume (col. G; 90°; N_2, 1.2 l/h).

1-*Bromo*-4-*trifluoromethyl-decafluorobicyclo*(2,2,1)*heptane* (IX)

1*H*-4-Trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (2.5 g) and methyl-lithium (1.5 *N* from MeBr) in ether were mixed in the usual way, bromine (9.0 g) added, and the solution stirred for a further ½ h at −60° and for 2 h at room temperature. The solution was then decolourized ($Na_2S_2O_3$) and the ethereal layer treated in the usual way to give a residue which was separated by GLC (col. M; 40°; N_2, 18 l/h) to give ether and 1-bromo-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (IX) (nc) (2.0 g) m.p. 39–40° (Found: C, 22.6; H, 0.0; Br, 18.3. C_8BrF_{13} requires C, 22.7; Br, 18.9%) *m/e* 422, 424 (C_8BrF_{13}); this bromide (IX) (0.4 g) and $LiAlH_4$ (0.5 g) in ether (70 ml) at 0° afforded 1*H*-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (0.25 g) with a correct IR spectrum.

4-*Trifluoromethyl-decafluorobicyclo*(2,2,1)*heptane*-1-*carboxylic acid* (X)

1*H*-4-Trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (2.0 g), methyl-lithium (1.5 *N*, from MeBr) in ether were mixed in the usual way and the solution treated with CO_2 in the manner described previously to give, after sublimation (14 mm Hg), 4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane-1-carboxylic acid monohydrate (X) (nc) (1.8 g) m.p. 78° (decomp.) (Found: C, 26.5; H, 0.5. $C_9HF_{13}O_2.H_2O$ requires C, 26.6; H, 0.7%), $\nu_{max.}$ *ca.* 3050 (hydrogen-bonded OH) and 1755 cm^{-1} ($>C=O$), *m/e* 325 (C_8HF_{12}), 212 (C_5F_8) and 44 (CO_2) and a base peak at 113 (C_3HF_4), its ^1H NMR spectrum consisted of a singlet at −0.6 τ. The acid (1.0 g) and a solution of diazomethane, prepared from *p*-tolyl sulphonyl methyl nitrosamide (2.14 g), in ether (15 ml) afforded methyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptan-1-carboxylate (0.7 g) (nc) b.p. 165° [purified by GLC (col. N; 90°; N_2, 3.5 l/h)] (Found: C, 29.7; H, 0.8. $C_{10}H_3F_{13}O_2$ requires C, 29.8; H, 0.8%), $\nu_{max.}$ 2970 (CH_3) and 1775 cm^{-1} ($>C=O$), *m/e* 402 ($C_{10}H_3F_{13}O_2$) and a base peak at 59 (CO_2CH_3), its ^1H NMR spectrum consisted of a sharp singlet at 6.0 τ.

A slurry of $LiAlH_4$ (0.2 g) in ether (15 ml) was added drop-wise to the ester (0.2 g) in ether (60 ml) at 0°. Treatment of this mixture in the usual manner gave 4-trifluoromethyl-decafluorobicyclo(2,2,1)hept-1-yl methanol, containing a small amount of ether, with a correct IR spectrum[7].

Decomposition of lithium 4-*trifluoromethyl-decafluorobicyclo*(2,2,1)*heptyl* (VI)

1*H*-4-Trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (2.0 g) and methyl-lithium (0.15 g; from MeI) in ether were mixed as before and the solution stirred for ½ h at −40°, and for 2 h under reflux. Further stirring overnight at room temperature was followed by the addition of 4 *N* HCl (25 ml). The ethereal layer gave, after the usual procedure, a residue which was shown by GLC (col. L; 100°; N_2, 4.5 l/h) to contain, besides ether, three minor short-retained components and one major and one minor long-retained component. Separation by semi-preparative scale GLC (col. N; 90°; N_2, 3.5 l/h) gave four fractions. Fraction (i) was a mixture (0.1 g) of three components. Two of these were identified by correlation of absorptions of the respective IR spectra as 1-methyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VIII) and 1*H*-4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XII). Mass spectrometry and several IR absorption bands not assigned to the two former compounds indicate the third component to be 1-methyl-4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XIII). Fraction (ii) was 1*H*-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (0.4 g), with a correct IR spectrum. Fraction (iii) was 1-iodo-4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XI) (nc) (1.1 g) b.p. 136–138°, $\nu_{\max.}$ 1750 cm^{-1} (s) ($-CF{=}CF-$), *m/e* 432 ($C_8F_{11}I$); this iodide (0.1 g), magnesium turnings (0.5 g) and a crystal of iodine in refluxing ether (75 ml) were treated, after 2 h, with 4 *N* HCl (10 ml), the ether layer evaporated (vac. jacketed col. 15 cm × 2.5 cm; glass helices) and the residue separated by semi-preparative scale GLC (col. N; 70°; N_2, 3.5 l/h) to give ether and 1*H*-4-trifluoromethyl-octafluorobicyclo(2,2,1)-hept-2-ene (XII) (0.05 g) with a correct IR spectrum. Fraction (iv) was 1-iodo-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VII) (0.5 g) with a correct IR spectrum.

1-*Bromo-4-trifluoromethyl-octafluorobicyclo*(2,2,1)*hept-2-ene* (XVII)

1*H*-4-Trifluoromethyl-octafluorobicyclo(2,2,1)heptane (II) (2.0 g) in ether (180 ml) at −40° was treated with methyl-lithium (0.18 g, from MeBr) and the temperature raised as in the previous experiment. Separation of the final ethereal residue by semi-preparative scale GLC (col. N; 60°; N_2, 3.5 l/h) gave three fractions besides ether. Fraction (i) was 1*H*-4-trifluoromethyl-octafluorobicyclo-(2,2,1)hept-2-ene (XII) (trace amount), with a correct IR spectrum. Fraction (ii) was 1-bromo-4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XVII) (nc) (0.7 g) b.p. 118–119° (Found: C, 25.1; H, 0.1. C_8BrF_{11} requires C, 24.9%), $\nu_{\max.}$ 1755 cm^{-1} ($-CF{=}CF-$), *m/e* 384, 386 (C_8BrF_{11}), 422–424 (vw) (C_8BrF_{13} in trace amounts); this olefin (0.2 g) in N_2 (5 l/h) was passed over CoF_3 at 100° to give 1-bromo-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (IX) (0.16 g) with a correct IR spectrum. Fraction (iii) 1*H*-4-trifluoromethyl-decafluorobicyclo(2,2,1)-heptane (0.4 g) (II) with a correct IR spectrum.

Decomposition of 4-*trifluoromethyl-decafluorobicyclo*(2,2,1)*hept*-1-*yl lithium in the presence of excess methyl-lithium. (a) Made from methyl iodide*

To an ethereal solution of 1*H*-4-trifluoromethyl-decafluorobicyclo(2,2,1)-heptane (II) (7.0 g) methyl-lithium (from MeI) was added until methane evolution ceased (400 ml), extra ethereal methyl-lithium (to give a total of 42 ml; 1.2 *N*) was then added, and after ½ h at −55°, ½ h at 25° and 1 h at 35°, the reaction mixture, in the usual way, afforded a residue which was separated by semi-preparative scale GLC (col. N; 70°; N_2, 3.5 l/h) to give ether and four product fractions. Fraction (i) was 1-methyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)-heptane (VIII) (0.5 g) with a correct IR spectrum. Fraction (ii) was 1*H*-4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XII) (nc) (1.7 g), m.p. 47–48°, $\nu_{max.}$ 1760 cm^{-1} (–CF=CF–), *m/e* 306 (C_8HF_{11}); its ^1H NMR spectrum consisted of a broad band at 5.6 τ; this olefin (0.1 g) in N_2 (3 l/h) was passed over CoF_3 at 130° to give 1*H*-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (0.1 g) with a correct IR spectrum. Fraction (iii) was 1*H*-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (trace amount) with a correct IR spectrum. Fraction (iv) was a mixture (2.5 g) of 1,2-dimethyl-4-trifluoromethyl-heptafluorobicyclo-(2,2,1)hept-2-ene (XVIII) and *endo*- and *exo*-1,6-dimethyl-4-trifluoromethyl-heptafluorobicyclo(2,2,1)hept-2-ene (XIX) (Found: C, 38.1; H, 2.2. $C_{10}H_6F_{10}$ requires C, 38.0; H, 1.9%); analytical GLC on columns HIGL and K at various temperatures and nitrogen flow-rates did not separate these olefins. They had $\nu_{max.}$ 2990, 2950, 2925 cm^{-1} (CH_3), 1760 cm^{-1} (–CF=CF–) and 1715 cm^{-1} (–CF=C(CH_3)–), *m/e* 316 ($C_{10}H_6F_{10}$), 216 ($C_8H_6F_6$), 220 ($C_7H_3F_7$) and 96 ($C_3H_3F_3$). Their ^1H NMR spectrum consisted of two broad bands centred at 8.2 τ (>C=C<(CH_3)) and 8.6 τ (⋗C–CH_3) in the relative intensity ratio of 4:6, respectively. Their ^{19}F NMR spectrum included bands in the relative intensity ratio of 4:1:1:1, respectively centred at 126.9 φ (⋗C–F in 2-substituted isomer) and 140.3 φ, 150.7 φ (⋗C–F in 6-substituted isomer) and 151.4 φ (⋗C–F in 6-substituted isomers).

(b) *Made from methyl bromide*

To a well-stirred solution of 1*H*-4-trifluoromethyl-decafluorobicyclo(2,2,1)-heptane (II) (2.0 g) in dry ether (200 ml) at —40°, methyl-lithium (0.36 g; from MeBr) was added slowly. Treatment of the reaction mixture as before gave a residue which was separated by semi-preparative scale GLC (col. N; 45°; N_2, 3.5 l/h) to give four fractions besides ether. Fraction (i) was 1-methyl-4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (VIII) (trace); fraction (ii) 1*H*,4-trifluoromethyl-octafluorobicyclo(2,2,1)hept-2-ene (XII) (trace); fraction (iii) 1*H*,4-trifluoromethyl-decafluorobicyclo(2,2,1)heptane (II) (trace). Fraction (iv) was a mixture (1.1 g) of 1,2-dimethyl-4-trifluoromethyl-heptafluorobicyclo(2,2,1)hept-2-ene (XVIII) and *endo*- and *exo*-1,6-dimethyl-4-trifluoromethyl-heptafluorobicyclo-(2,2,1)hept-2-ene (XIX) in the ratio of 17:3, respectively, as shown by ^{19}F NMR spectroscopy. Compounds (i)–(iv) had correct IR spectra.

ACKNOWLEDGEMENTS

The authors thank colleagues as before[2] and the M.O.T. for a Maintenance Grant (to K.N.W.).

REFERENCES

1 Part III. S. F. Campbell, J. M. Leach, R. Stephens, J. C. Tatlow and K. N. Wood, *J. Fluorine Chem.*, *1* (1971) 103.
2 Part. II. S. F. Campbell, J. M. Leach, R. Stephens and J. C. Tatlow, *J. Fluorine Chem.*, *1* (1971) 85.
3 D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1964) 3035.
4 Part I. S. F. Campbell, R. Stephens and J. C. Tatlow, *Tetrahedron*, *21* (1965) 2997.
5 W. B. Hollyhead, R. Stephens, J. C. Tatlow and W. T. Westwood, *Tetrahedron*, *25* (1969) 1777.
6 A. Streitwieser, Jr. and D. Holtz, private communication.
7 P. J. N. Brown, R. Stephens, J. C. Tatlow, J. R. Taylor and K. N. Wood, unpublished work.