Journal of Fluorine Chemistry, *24* (1984) 509–522

Received: May 25, 1983; accepted: October 17, 1983

POLYFLUORO-COMPOUNDS BASED ON THE CYCLOHEPTANE RING SYSTEM. PART 6. BICYCLIC COMPOUNDS DERIVED FROM NONAFLUOROCYCLOHEPTA-1,3-DIENES AND FROM OCTAFLUOROCYCLOHEPTA-1,3,5-TRIENE

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SUMMARY

1H-, 2H-, and 5H- Nonafluoro- and 1H,4H-octafluoro-cyclohepta-1,3 diene afforded the corresponding H-substituted polyfluorobicyclo(3,2,0)-hept-6-enes by cross-ring bond formation between positions 1 and 4. Octafluorocyclohepta-1,3,5-triene similarly gave octafluorobicyclo-(3,2,0)hepta-2,6-diene. By passage over cobalt(III) fluoride at 100 °C, the 1H-bicyclo-6-ene gave 1H-undecafluorobicyclo(3,2,0)heptane and thence the corresponding fluorocarbon. The bridgehead hydrogen of the 1H-bicyclo-ane was sufficiently acidic to exchange for deuterium with deuterium oxide, alone or containing some potassium hydroxide, but longer exposure to aqueous potash gave decafluorobicyclo(3,2,0)hept-1(5)-ene. This was oxidised by potassium permanganate in acetone to give decafluoro-1,5-dihydroxy-8-oxabicyclo(3,2,1)octane (hydrated), which underwent methylation by diazomethane to the corresponding 1,5-dimethoxy-compound. A Diels-Alder reaction between ethylene and 1H-nonafluorocyclohepta-1,3-diene afforded 1H,8H,8H,9H,9H-nonafluoro-bicyclo(3,2,2)non-6-ene. Cobalt (III) fluoride at 300°C converted this principally to 1H-pentadecafluoro-bicyclo(3,2,2)nonane. The bridgehead hydrogen of this was exchanged for deuterium using deuterium oxide alone or containing potassium hydroxide. However, dehydrofluorination occurred with bases, though an olefin could not be isolated.

0022-1139/84/$3.00

INTRODUCTION

The previous paper in this series [1] detailed the preparation of some hydrogen-containing fluorocycloheptadienes (I- IV: see Scheme) and thence octafluorocyclohepta-1,3,5-triene(V). We had previously shown [2] that decafluorocyclohepta-1,3-diene underwent cross-ring bond formation, under the influence of ultraviolet light or of heat, to give decafluorobicyclo(3,2,0)hept-6-ene. This conversion paralleled the known [3] reaction of this type undergone by cyclohepta-1,3-diene.

The range of polyfluorobicyclo(3,2,0)heptenes has now been extended by synthesis of the examples (VI-IX) derived from the above mentioned cycloheptadienes (I-IV), and also (X) from the perfluoro-triene (V). Included among the products made were the first polyfluorides of this bicyclo-series with hydrogen on a bridgehead position.

The Diels-Alder reaction between ethylene and decafluorocyclohepta-1,3-diene had earlier given [2] the first polyfluoride of the bicyclo(3,2,2)nonane series to be made. A similar reaction has now been applied to 1H-nonafluorocyclohepta-1,3-diene (I), to give the first members of this bicyclo-series with bridgehead hydrogen.

Studies on polyfluorides of the bicyclo(2,2,1)heptane series [4] and on those of the bicyclo(2,2,2)octane series [5], have shown that hydrogen substituents located at bridgehead positions are incipiently acidic [6]. This is an interesting effect in its own right; further, however, replacement reactions on such compounds are of considerable synthetic value. When it was started, the primary objective of the present work was to confirm the structures of the new cyclohepta-diene and -triene precursors. Though this was done, the synthetic sequences and the spectroscopic parameters of compounds I-V were in fact conclusive in themselves [1]. The second objective of the work was much more significant therefore; it was a preliminary study of the acidities of bridgehead hydrogen substituents in the polyfluoro-derivatives of two further bicyclic series.

RESULTS AND DISCUSSION

The bicyclo(3,2,0)heptenes were made by room-temperature photoisomerisations promoted by ultraviolet light. Though reaction times were long, usually several days, the recoveries of products were very good.

1H-Nonafluorocyclohepta-1,3-diene (I) was the most readily available precursor and its photo-isomer could be made in fair quantities. It clearly had the structure 1H-nonafluorobicyclo(3,2,0)hept-6-ene (VI), as shown by an infrared band at 1785 cm^{-1}, and appropriate nmr peaks: at 6.44τ for tertiary hydrogen; in the ^{19}F spectrum at 180.4 (1 tertiary F), 108.3 and 117.6 (2 vinylic F), 102-132 (overlapping AB quartets arising from 3 $>CF_2$ groups) (see Table for all n.m.r. data).

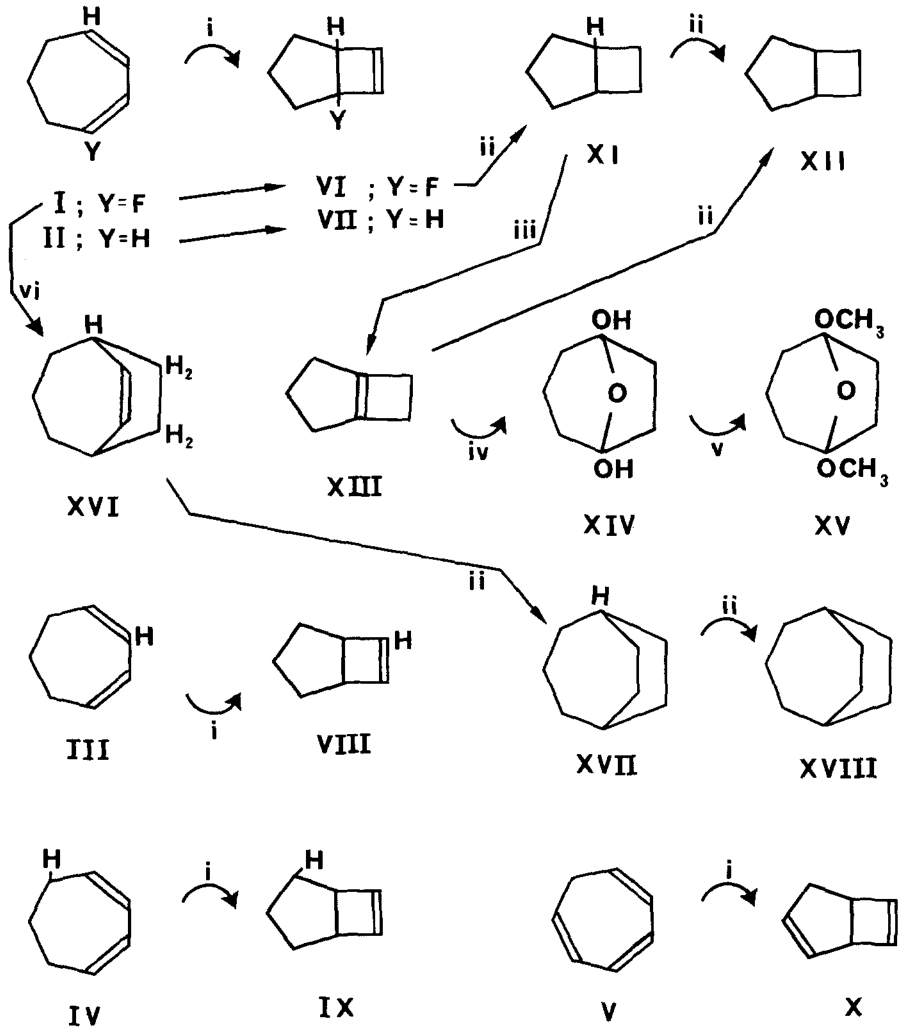
1H,4H-Octafluorocylohepta-1,3-diene (II) was isomerised to 1H,5H-octafluorobicyclo(3,2,0)hept-6-ene (VII). The nmr spectra showed a symmetrical structure, with one hydrogen peak only (tertiary position), but there was no tertiary fluorine; there was one low-field absorption for vinylic fluorine and two distinct AB systems (intensity ratios 1:2:1).

2H-Nonafluorocyclohexa-1,3-diene (III) was photoisomerised to a known compound, 6H-nonafluorobicyclo(3,2,0)hept-6-ene (VIII). This had been made previously [2], but only in trace amount, by reaction of decafluorobicyclo(3,2,0)hept-6-ene with sodium borohydride. The compound had nmr peaks in accord with the structure.

5H-Nonafluorocyclohepta-1,3,-diene (IV) gave, on irradiation by uv, 2H-nonafluorobicyclo(3,2,0)hept-6-ene (IX) as a mixture (55 : 45) of endo- and exo-stereoisomers. There was a characteristic [7] infrared peak for -FC=CF- in a fluorocylobutene, and the nmr spectra showed two different sets of peaks for >CHF with the typical doublet splitting.

Octafluorocyclohepta-1,3,5-triene (V) was irradiated in solution in cyclohexane under rigorously dry conditions, and afforded octafluorobicyclo(3,2,0)hepta-2,6-diene (X). This had two distinct infrared double bond peaks, and ^{19}F nmr peaks for all the fluorine positions present (2 tertiary, 4 vinylic and $>CF_2$). This product was analogous to that obtained by irradiation of cyclohepta-1,3,5-triene [8].

1H-Nonafluorobicyclo(3,2,0)hept-6-ene (VI) was passed over cobalt(III) fluoride at 100°C to give a good recovery of the saturated analogue, 1H-undecafluorobicyclo(3,2,0)heptane (XI). The bridgehead hydrogen was fluorinated only sluggishly, as with other systems [4,5]: at 250°C, the known [2] bicyclic fluorocarbon (XII) was formed, but the major product was still the 1H-compound (XI).



Reagents : i, uv light ; ii, CoF_3 ; iii, KOH ; iv, $KMnO_4$;

v, CH_2N_2 ; vi, $CH_2{=}CH_2$.

ALL UNMARKED BONDS ARE TO FLUORINE

Scheme

1H-Undecafluorobicyclo(3,2,0)heptane (XI) was shaken with deuterium oxide at 20°C, and after 30 minutes had exchanged deuterium for hydrogen to the extent of 12%, as measured by mass spectrometry. Comparably, the isomeric 1H-undecafluoro-bicyclo(2,2,1)heptane had not taken up any deuterium (not surprisingly, from other results)[6]. This level of uptake into compound XI indicates a relatively high rate of exchange of bridgehead hydrogen. Though comparisons between heterogeneous systems are very difficult, nevertheless this result must mean that a very acidic >C-H group is present in compound XI [<u>cf</u>. 6]. When deuterium exchange by the two isomeric 1H-bicycloheptanes was carried out using deuterium oxide containing potassium hydroxide, the products isolated from both reactions showed deuterium contents of 15-20%. However, whilst the product from the bicyclo(2,2,1)heptane had undergone no dehydrofluorination, [<u>cf</u>. 9], that from the (3,2,0)heptane (XI) contained a significant additional component. Further experiments on compound (XI) using aqueous potassium hydroxide showed that it could be dehydrofluorinated quite readily to give a fluorocarbon olefin product (XIII). Unfortunately therefore, the high acidity of this 1H-compound, (XI) though very interesting and significant, is not readily exploitable, particularly synthetically. Exchange reactions or metallations at the >C-H bond of compound XI will always be swamped by dehydrofluorination, which does not happen with polyfluorobicyclo-(2,2,1)-heptanes [9,4] and (2,2,2)-octanes [5].

Returning to the controlled dehydrofluorination of the 1H-(3,2,0)-bicycloheptane (XI), it occurred quite readily and under mild conditions using relatively dilute aqueous potassium hydroxide. The product contained one major (XIII) and two very minor constituents, one of the latter being recovered XI. The major product (XIII) had only 3 peaks (intensity ratio 2:2:1) in its ^{19}F nmr spectrum,with no tertiary F absorption and there was a very weak infrared double bond peak at 1670 cm^{-1}.

Fluorination over cobalt(III) fluoride at 100°C gave the saturated fluorocarbon XII. The olefinic product was therefore decafluorobicyclo-(3,2,0)hept-1(5)-ene (XIII). The second trace product was not isolated in sufficient quantity for identification; it had strong infrared absorption at 1788 cm^{-1}.

Other factors being equal, in dehydrofluorination reactions, fluorine is lost more readily from a tertiary position than from $>CF_2$[10,11]. The stereochemistry of the ring fusion positions in the starting material XI would seem to allow a reasonable cis-elimination pathway, involving the hydrogen at C_1 and the tertiary fluorine at C_5. Dehydrofluorinations of both trans- and cis- arranged hydrogen and fluorine proceed quite readily from polyfluorocyclopentanes [12]. Therefore, from compound XI, olefin XIII should be formed in preference to either of the isomeric 1(2)- and 1(7)-enes. Further, there was found to be a very rapid rearrangement [10] of hexadecafluorobicyclo(4,4,0)dec-1(2)ene, to give the isomeric 1(6)-ene, catalysed by the fluoride ion liberated during the dehydrofluorination. This suggests therefore that even if dehydrofluorination of compound XI had given preferentially the other possible olefinic products, the 1(2)- or 1(7)-enes, they would have rearranged under the reaction conditions used, so that the 1(5)-ene (XIII) would be the product actually isolated.

Oxidation of decafluorobicyclo(3,2,0)hept-1(5)-ene (XIII) was carried out using potassium permanganate in acetone as oxidant. This is well known [13] to give polyfluoro-dibasic acids from polyfluorocycloalkenes with double bonds of the type -CF=CF-, and has given [14] a keto-acid from 1-methylnonafluorocyclohexene, though not from 1-trifluoromethylnonafluorocyclohexene [11]. From the bicyclo-ene (XIII) there was isolated a crystalline solid (XIVa), with elemental analysis corresponding to the formula $C_7H_4F_{10}O_4$. It had two distinct -OH absorptions in the infrared, and mass spectrometry gave a top mass peak corresponding to the formula $C_7H_2F_{10}O_3$ (XIV). Methylation of compound XIVa using diazomethane in ether gave a dimethoxide (XV) as a low melting solid, analysing as $C_9H_6F_{10}O_3$. It appeared therefore that oxidation of compound XIII cleaved the 1(5)-ene bond completely, to give species based on the decafluorocyclohepta-1,4-dione structure. The latter is geometrically well suited to react with a molecule of water to give decafluoro-1,5-dihydroxy-8-oxabicyclo(3,2,1)octane (XIV), though the product actually isolated (XIVa) contained a further molecule of water in its structure.
It was probably a hydrate, with the second water molecule present as such in the crystal lattice, rather than being formally bonded chemically to give a tetra-ol with loss of the oxygen bridge. In any event, the product of methylation had the characteristics of a dimethyl ether of structure XIV, with an oxygen bridge present.

Oxidation of hexadecafluorobicyclo(4,4,0)dec-1(6)ene by permanganate in acetone did not cleave the double bond [15], the product isolated being the bis-hydroxylated product, hexadecafluorobicyclo(4,4,0)-decane-1,6-diol. However, there is less steric strain in this bicyclodecene structure than in the bicycloheptene (XIII), so the rupture of the original olefinic bond in the latter, but not in the former, is understandable.

The Diels-Alder reaction between 1H-nonafluorocyclohept-1,3-diene (I) and ethylene under pressure gave an excellent recovery of product, considering the conditions used (300°C for 7½ days). These were even more drastic than for perfluorocyclohepta-1,3-diene [2], and significantly more so than for 1H-heptafluorocyclohexa-1,3-diene [16]. Presumably, the geometry of the cycloheptadiene ring is such that more deformation is needed for successful ring closure.

The product was 1H,8H,8H,9H,9H-nonafluorobicyclo(3,2,2)non-6-ene (XVI) as shown by analysis and spectroscopic data (^{1}H nmr showed three types of hydrogen, intensity ratio 2:2:1, and ^{19}F nmr a tertiary fluorine). Fluorination of compound XVI by cobaltic fluoride at 300°C gave mainly 1H-pentadecafluorobicyclo(3,2,2)nonane (XVII) together with some perfluorobicyclo(3,2,2)nonane (XVIII), into which compound XVII could be converted. There was also a fraction which could well have been a 6H-pentadecafluoride. The major fluorination product was saturated, and showed a bridgehead hydrogen and a bridgehead fluorine absorption in its nmr spectra, indicating structure XVII.

The acidity of the bridgehead hydrogen in compound XVII was demonstrated by its exchange for deuterium on being shaken with deuterium oxide in a sealed ampoule at 100°C for 5½ hours (uptake 9%), and when it was shaken with potassium hydroxide in deuterium oxide (1:1) at 20°C for 5½ hours (uptake 19%). However there were signs of decomposition in the latter reaction, though no unsaturated product could be isolated. Heating the system at 100°C caused complete degradation, as did passage through molten potash. Treatment of XVII with methyl-lithium in ether gave methane evolution of about half that corresponding to complete metallation; reaction with deuterium oxide then gave compound XVII, about 88% deuterated, but in less than 25% recovery. Attempts at other exchanges after lithiation were unsuccessful, complex mixtures resulting.

It seems therefore that though the bridgehead hydrogen compound (XVII) shows acidity, dehydrofluorination of some sort proceeds quite readily, this last in complete contrast to the 1H-analogues of the 2,2,1-heptane [9,4]and 2,2,2-octane series [5]. Presumably, the extra carbon atom in the 3,2,2-nonane compounds allows sufficient ring flexing to permit a bridgehead olefin to form relatively readily, though it is clearly not very stable. It seems fairly general now, that a bridgehead hydrogen in a polyfluoride of a bicyclic carbon series shows acidity, and is readily exchanged, but for easy synthetic exploitation of this effect, the complete absence of any facile elimination pathway is necessary.

EXPERIMENTAL

General

Spectroscopic measurements were done as in Part 5 [1]. Glc was also as described there; an additional preparative column (G) was used, 4.8 m 35 mm diam., packed with polyethylene glycol (Carbowax 6000)/30S Celite (1:5).

Photoisomerisations of polyenes of the cycloheptane series to give bicyclo(3,2,0)heptenes

(a) 1H-Nonafluorocyclohepta-1,3-diene (I) Compound I (7.0g) was sealed in a quartz flask in a nitrogen atmosphere and irradiated by ultraviolet light (Hanovia medium pressure lamp) for 150 hours. The yellow product was distilled to give 1H-nonafluorobicyclo(3,2,0)hept-6-ene (VI) nc (6.5g), b.p. 83°C (Found: C,32.6; H,0.7. C_7HF_9 requires C,32.8; H,0.4%); M/e 256 (M); ir 2990 (w; C-H), 1785 (s, CF=CF) cm^{-1}.

(b) 1H,4H-Octafluorocyclohepta-1,3-diene (II) This (1.5g) after treatment as in expt. (a), followed by distillation at 15 mm Hg from P_2O_5, afforded 1H,5H-octafluorobicyclo(3,2,0)hept-6-ene (VII) nc (1.2g),b.p. 109-110°C (Found M/e 238:M); ir 2980 (w), 1785 (s).

(c) 2H-Nonafluorocyclohepta-1,3-diene (III) Irradiated as in (a) for 70 h, compound III (0.4g) afforded 6H-nonafluorobicyclo(3,2,0)hept-6-ene (VIII) (0.36g), b.p.80-81°C, m.p. ca 20°C (Found: C, 32.8; H, 0.5; F, 66.9%); M/e 256 (M); ir 3120 (w), 1665 (s) (spectrum corresponding to that for the earlier specimen [2] though the values cited were inaccurate).

(d) 5H-Nonafluorocyclohepta-1,3-diene (IV) This diene (0.7g), irradiated for 100 h, followed by distillation as in (b), afforded endo- and exo-2H-nonafluorobicyclo (3,2,0)hept-6-ene (IX) (0.55g) (Found M/e 256: M); ir 2990 (w), 1800 (s).

(e) Octafluorocyclohepta-1,3,5-triene (V) This (0.2g) in dry cyclohexane (3 cm^3) was irradiated for 24 h. Glc separation (D, 100°, 6) gave: (i) octafluorobicyclo (3,2,0)hepta-2,6-diene (X) nc (0.11g), b.p. 73-74°C (Found: C,35.3; F,64.5. C_7F_8 requires C, 35.6; F,64.4%); M/e 236 (M), 186 ($M-CF_2$); ir 1780 (s), 1750 (s): (ii) cyclohexane.

Fluorination of 1H-nonafluorobicyclo(3,2,0)hept-6-ene (VI)

Compound VI (4.1g) was vapourised in a stream of nitrogen (2.5 lh^{-1}) and passed during 30 min through a standard stirred reactor [17] filled with cobalt(III) fluoride (150g) and held at 100°C. The nitrogen flow was continued for 2 hours further, the product (4.1g) being collected in a glass trap at -178°C. The product was distilled at 15 mm Hg pressure from P_2O_5 to give 1H-undecafluorobicyclo(3,2,0)heptane (XI) nc (4.0g), b.p. 82-83°C (Found: C, 28.5; H,0.9 : C_7HF_{11}requires C, 28.6; H,0.3%); M/e 294 (M); ir 2990 (w).

The 1H-bicyclo-ene (VI) (0.9g) was fluorinated similarly at a reactor temperature of 250°C. The two-component product was separated by glc (A, 75°, 3.5) to give: (i) dodecafluorobicyclo(3,2,0)heptane (XII) (0.11g) identical by glc and ir with an earlier sample [2]: (ii) compound XI (0.59g).

Dehydrofluorination of 1H-undecafluorobicyclo(3,2,0)heptane (XI)

The title compound (1.8g) and a solution of potassium hydroxide (0.2g) in water (3.5g) were shaken together in a stoppered flask at 20°C for 4.5 hours. The organic layer was separated off, distilled at 15 mm Hg pressure from P_2O_5, and separated by glc (A, 85°, 5) to give: (i) decafluorobicyclo(3,2,0)hept-1(5)-ene(XIII) nc (0.7g), b.p. 63-64°C (Found; C, 30.5. C_7F_{10} requires C, 30.7%); M/e 274 (M); ir 1670 (w): (ii) unreacted (XI) (trace; glc and ir): (iii) unknown (trace), ir 1788 (s).

When the 1(5)-ene (XIII) (0.3g) was passed over CoF_3 at 100°C as before, the saturated fluorocarbon XII (0.15g; glc and ir) was obtained.

Oxidation of decafluorobicyclo(3,2,0)hept-1(5)-ene (XIII)

Olefin XIII (1.8g) was added slowly to stirred potassium permanganate (1.2g) in dry acetone (50 cm^3) and stirring continued for 1 hour further at 15°C. Water (20 cm^3) was added, the solution decolourised by passage of sulphur dioxide gas and the acetone evaporated off at reduced pressure. The residual solution was acidified and extracted with ether (3 x 50cm^3). The extracts were dried ($MgSO_4$) and the ether evaporated off to leave a brown oil (1.0g). Distillation (70°C/15mm) onto a cold finger gave a solid (0.9g), which was recrystallised from carbon tetrachloride to give decafluoro-1,5-dihydroxy-8-oxabicyclo(3,2,1)octane hydrate (XIVa) nc, (0.63g) m.p. 70-71°C (Found: C, 24.8; H, 0.9; F, 55.6. $C_7H_2F_{10}O_3.H_2O$ requires C, 24.6; H, 1.2; F, 55.5%); M/e 324 ($C_7H_2F_{10}O_3$); ir 3500 (s), 3140 (b,s).

Methylation of compound XIVa

To the hydrated diol (XIVa) (0.5g) in dry diethyl ether (20 cm^3) was added dropwise at 0°C ethereal diazomethane, until effervescence ceased. After being kept for 14 hours further, the solution was dried ($MgSO_4$) and the bulk of the ether distilled off through a distillation column (15 cm x 2 cm) packed with glass helices. The residual liquid (0.43g), by glc (D, 110°, 4) afforded: (i) ether and ethanol: (ii) decafluoro-1,5-dimethoxy-8-oxabicyclo(3,2,1)octane (XV) nc (0.25g), m.p. 38°C (Found: C, 30.4; H, 2.0. $C_9H_6F_{10}O_3$ requires C, 30.7; H, 1.7%); M/e 352 (M).

Diels-Alder reaction of 1H-nonafluorocylohepta-1,3-diene (I) with ethylene

In a rocking autoclave, diene I (18g) and quinol (0.1g) were maintained at 300°C in an atmosphere of ethylene (60 atm. pressure) for 180 hours. The excess of ethylene was released, the autoclave cooled, and the pale cream solid residue sublimed (100°C/7mm Hg) to give 1H,8H,8H,9H,9H-nonafluorobicyclo(3,2,2)non-6-ene (XVI) nc (18g), m.p. 135-136°C (Found: C, 37.9; H, 1.7. $C_9H_5F_9$ requires C, 38.0; H, 1.8%); M/e 284 (M); ir 3000-2850, 1760.

Fluorination of bicyclononene XVI

Compound XVI (10.5g) was swept by a nitrogen stream (5 lh^{-1}) into the cobalt fluoride reactor at 300°C. The emergent vapours were passed through a heated tube packed with sodium fluoride pellets, and the organic products (13g) trapped at -178°C. The solid product from two such runs was dissolved in ether, and a proportion (12g) was separated by glc (G, 60°,20) to give: (i) perfluorobicyclo(3,2,2)nonane (XVIII) (1.1g) (not fully characterised): (ii) a mixture of ether, fluorocarbon XVIII, and the material of fraction (iii) (1.8g): (iii) suspected 6H-pentadecafluorobicyclo(3,2,2)nonane (2.3g) (not examined further): (iv) 1H-pentadecafluorobicyclo(3,2,2)nonane (XVII) nc (4.9g) m.p. 146-7°C (sealed tube) (Found: C, 27.7; H, 0.3. C_9HF_{15} requires C, 27.4; H, 0.3%); M/e 394 (M), 375 (M-F); ir 2970.

When the 1H-compound (XVII) was passed through the cobalt fluoride reactor at 300°C, the product was largely unchanged XVII but also contained fluorocarbon XVIII (<10%).

Deuterations of bridgehead hydrogen compounds

(a) 1H-Undecafluorobicyclo(3,2,0)heptane (XI)

(i) Compound XI (0.2g) and deuterium oxide (1.0g) were shaken together mechanically in a stoppered glass tube at 20°C for 30 min. After separation, the organic layer was distilled in vacuo from P_2O_5. Mass spectrometry indicated it to be compound XI, containing its deuterated analogue (12%).

Under comparable conditions, 1H-undecafluorobicyclo(2,2,1)heptane gave a deuterium content within the probable experimental error of the measurement.

(ii) Compound XI (0.2g), potassium hydroxide (0.05g), and deuterium oxide (2.0g) treated similarly gave a deuterium content of 14%, but some of olefin XIII was also present: 1H-undecafluorobicyclo(2,2,1)heptane under these conditions gave a deuterium uptake of 19%, with no other products.

(b) 1H-Pentadecafluorobicyclo(3,2,2)nonane (XVII)

(i) Compound XVII (0.15g) and deuterium oxide (1.0g) were shaken together in a sealed glass ampoule at 100°C for 5½ hours. After work-up as above the deuterium uptake was 9%.

(ii) Compound XVII (0.15g), potassium hydroxide (0.8g) and deuterium oxide (0.8g) were shaken together in a glass tube at 20°C for 5½ hours. The deuterium uptake was 19%, but there were signs of some darkening and decomposition. Heating the system at 100°C caused complete decomposition, as did passage of compound XVII through molten potassium hydroxide.

TABLE

Nmr Spectra of New Compounds*

Compound No.		Chemical Shift	Relative Intensity	Position in Formula	Coupling
VI	F	108.3	1	7	c
		117.6	1	6	c
		102.3-132.3	6	2,3,4	overlapping AB s
		180.4	1	5	b
	H	6.44	-	1	b
VII	F	109.0	1	6,7	b
		103.6, 117.8	2	2,4	AB, J= ca 240
		103.8, 128.3	1	3	AB, J= ca 230
	H	6.42	-	1,5	b
VIII	F	87.0	1	7	c
		117.1, 141.9	2	2	AB, J= 260
		123.4, 132.2	2	3	AB, J= 260
		123.4, 134.3	2	4	AB, J= 260
		188.3	1	1	c
		189.8	1	5	c
	H	4.25	-	6	dd, J= 8.5 & 3.5
IX	F	110.9-138.5	-	3,4,6,7	overlapping
2 isomers, approx. 55 : 45		176.7	-	1,5	c
		189.7	-		c
		193.0	-		c
		212.6	-	2	d, J= 55
		223.2	-	2	d, J= 55
	H	4.35	-	2	d, J= 55
		4.60	-	2	d, J= 55

*Figures for ^{1}H are in τ units relative to tetramethylsilane, and those for ^{19}F in ppm to high field of trichlorofluoromethane, both internal references.

TABLE (cont.)

Compound No.		Chemical Shift	Relative Intensity	Position in Formula	Coupling
X	F	113.8	1	7	t, J= 11.3
(C_6D_6)		114.6, 117.3	2	4	AB,J= 255
		123.1	1	6	ct
		141.4	1	2	c
		153.5	1	3	ct
		179.5	1	1	ctd
		190.6	1	5	c
XI	F	105-148	10	2,3,4,6,7	overlapping AB s
		198.5	1	5	c
	H	5.75	-	1	b
XIII	F	108.6	2	2,4	c
		113.3	2	6,7	c
		125.6	1	3	c
XIVa	F	123.5	2	2,3,4,6,7	c
(CD_3COCD_3)		125.9, 131.8	2		AB, J= 266
		127.5, 133.4	1		AB, J= 282
	H	4.25			b
XV	F	118.7-141.0	3	2,3,4,6,7	overlapping AB s
($CDCl_3$)		125.8, 133.4	2		AB, J= 272
	H	6.26			s
XVI	F	109.2-149.6	8	2,3,4	overlapping (CF_2 and CF=CF)
		187.2	1	5	b
	H	7.94	2	7,8	b
		7.48	2		b
		6.78	1		b

TABLE (cont.)

Compound No.		Chemical Shift	Relative Intensity	Position in Formula	Coupling
XVII	F	92-129.5	-	2,3,4,6,7,8,9	overlapping AB s
		183.5	-	5	b
	H	5.8	-	-	b

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