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POLYFLUORO-COMPOUNDS BASED ON THE CYCLOHEPTANE  
RING SYSTEM. PART 3. BICYCLIC COMPOUNDS MADE  
FROM DECAFLUOROCYCLOHEPTA-1,3-DIENE

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SUMMARY

Decafluorocyclohepta-1,4- and -1,3-diene and decafluorobicyclo(3,2,0)hept-6-ene were interconverted at ca 460°, over packings such as sodium fluoride pellets or iron gauze. The 1,3-diene was converted by uv irradiation to the bicyclohept-6-ene, which underwent oxidation to octafluorocyclopentane-1,2-dicarboxylic acid, and saturation by cobalt(III) fluoride to the bicycloheptane, whilst nucleophilic addition-elimination gave the 6H- and 6H,7H-bicyclo-6-enes (from NaBH<sub>4</sub>), and the 6-methoxy-6-ene (from MeOH/KOH). Decafluorocyclohepta-1,3-diene in a Diels-Alder reaction with ethylene afforded 6H,6H,7H,7H-decafluorobicyclo(3,2,2)non-8-ene. This adduct was oxidised to 1,2,2,3,3,4,4,5-octafluorocycloheptane-1,5-dicarboxylic acid, whilst cobalt(III) fluoride at 180° fluorinated it to a mixture of 6H,6H-tetradeca- and 6H-pentadeca-fluorobicyclo(3,2,2)nonane. The latter with aqueous potassium hydroxide afforded tetradecafluorobicyclo(3,2,2)non-6-ene.

INTRODUCTION

This paper describes some reactions of decafluorocyclohepta-1,3-diene [1] leading to bicyclic structures. The reactions were extensions of those carried out on other systems. Double bond shifts are well known amongst fluorocarbon olefins, e.g. the interconversion of polyfluorocyclohexa-1,3- and -1,4-dienes [2], and the double bond migrations of perfluoroenes catalysed by fluoride ion [3]. Also well-known are the thermolyses

and photolyses of fluorocarbon alka-1,3-dienes to give cyclobutenes [4]: applied to octafluorocyclohexa-1,3-diene, this process affords octafluorobicyclo[2,2,0]hex-2-ene [5]. Also, the Diels Alder reaction has been carried out between ethylene and polyfluorocyclohexa-1,3-dienes, leading to fluoro-bicyclo(2,2,2)octanes [6].

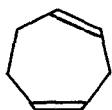
This paper describes the interconversion of decafluorocyclohepta-1,4- and -1,3-diene, and the syntheses of bicyclo-compounds by the two types of process outlined above.

## RESULTS AND DISCUSSION

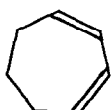
Perfluorocyclohepta-1,4-(I) and -1,3-diene(II) [1], were found to interconvert over sodium fluoride heated to 350-500°, the optimum being around 460°. However, a third component (III) was present in all cases, and sometimes predominated. Use of iron gauze gave a similar result, but iron oxide was less satisfactory. The new product (III) gave II and traces of I when it was itself passed at similar temperatures over sodium fluoride or glass helices. Except when it was the starting material, the 1,4-diene(I) was the minor constituent. Diene II had been converted completely to compound III after being irradiated by uv light for 1 week at 15°.

Compound III analysed as  $C_7F_{10}$ , had an ir band at 1780 (C=C), and the  $^{19}F$  nmr spectrum showed 4 sets of peaks, attributable to tertiary fluorine, vinylic fluorine, and two types of  $>CF_2$ . This established that compound III was decafluorobicyclo(3,2,0)hept-6-ene (see Scheme for all structures). Oxidation confirmed this structural allocation: permanganate in acetone afforded a mixed acidic product, from which the dianilinium and bis-S-benzylthiouronium salts were made. The presence of the hexafluoroglutaric acid salt in each mixture was demonstrated by analysis and ir. Oxidation of III by potassium permanganate in dilute sulphuric acid solution gave a crude syrupy acid, the  $^{19}F$  nmr spectrum of which had two sets of peaks in the  $>CF_2$  region, and one for tertiary fluorine, in intensity ratio 2:1:1, indicating structure IV. This acid gave a bis-S-benzylthiouronium salt(IVa) analysing as the derivative of an octafluorocyclopentane dicarboxylic acid.

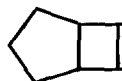
Clearly, the  $C_7F_{10}$  structures, I,II, and III, are in equilibria through the 1,3-diene II. Dienes I and II interconvert through a fluorine shift. Bond formation between positions 1 and 4 in diene III gives the bicyclic structure, by the 1,3-diene  $\rightarrow$  cyclobutene conversion, the 7-membered ring not offering much resistance from strain. Both reactions are reversible.



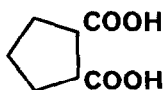
I



II



III



IV



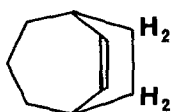
V



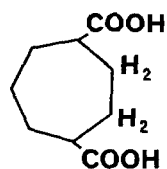
VI R = H  
VII R = F



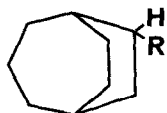
VIII



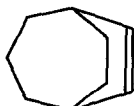
IX



X



XI R = F  
XII R = H



XIII

All  
unmarked  
bonds  
are to  
FLUORINE

SCHEME

Bicyclo-heptene III underwent reactions typical of those of double bonds in fluoro-compounds. Cobalt(III) fluoride at 160° gave the corresponding saturated bicyclic fluorocarbon (V).

Sodium borohydride in diglyme gave a stepwise addition-elimination sequence, 6H,7H-octafluorobicyclo(3,2,0)hept-6-ene(VI) being the major product, but the 6H-nonafluoride(VII) being isolated in small amount. Methanol/potassium hydroxide afforded the 6-methoxyhept-6-ene(VIII). All products were identified by analysis or mass spectrometry and spectroscopic data.

Diels-Alder reactions on decafluorocyclohepta-1,3-diene(II) were first done successfully using methyl acrylate and methyl vinyl ketone as co-reactants, but the products could not be purified satisfactorily. The reaction between diene II and ethylene proceeded smoothly at 250-275°, to give a good recovery of a crystalline adduct (IX). This had the requisite analytical data and spectroscopic parameters, including  $^{19}\text{F}$  peaks at 187 (tertiary fluorine) and 147.5 (vinylic fluorine in a cycloheptene ring) for the expected product (IX). Oxidation by potassium permanganate in acetone of adduct IX gave a crude acidic product, with  $^{19}\text{F}$  nmr peaks consistent with a cycloheptane dicarboxylic acid structure (X). From this was made the crystalline bis-S-benzylthiuronium salt(Xa) which analysed correctly. The bicyclo(2,2,2)octene analogue gave a corresponding acid [6].

Fluorination of adduct IX by cobalt(III) fluoride at 180° gave a major and minor isolatable product, together with a trace of a third. The major one was 6H-pentadecafluorobicyclo(3,2,2)nonane(XI), as shown by analysis and nmr (a fluorine peak at 215 and a proton peak at 4.5, both broad doublets, typical of  $>\text{CHF}$ ; two tertiary fluorines at 202 and 209). However, it was not clear whether XI was the endo- or exo-isomer. The trace product had nmr spectra strongly suggesting that it was the second stereoisomer of structure XI, but insufficient was present to allow isolation. The minor fluorination product was 6H,6H-tetradecafluorobicyclo(3,2,2)nonane(XII), as shown by analysis and  $^{19}\text{F}$  nmr peaks for tertiary fluorine at 189 and 209 (nothing present attributable to  $>\text{CHF}$ ). Though  $>\text{CH}_2$  groups are seldom present in the fluorination products from single ring carbocycles, two products containing them were found in significant proportions when polyfluorobicyclo(2,2,2)octanes were synthesised [7].

The 6H-bicyclononane(XI) was dehydrofluorinated by aqueous potassium hydroxide to give tetradecafluorobicyclo(3,2,2)non-6-ene(XIII).

## EXPERIMENTAL

Gas liquid chromatography and spectroscopy were done as in Part 2 [1].

Thermal Reactions of Decafluorocycloheptadienes.

(a) The 1,3-Diene(II) Diene II (2.5 g) was vapourised in a nitrogen stream ( $2 \text{ l h}^{-1}$ ) and passed during 30 min. through a glass tube (600 mm x 28 mm diam.) packed with sodium fluoride pellets, and heated electrically to  $460^\circ$ . Nitrogen was passed for 1 h further, the product (1.7 g) being collected in a trap cooled by liquid nitrogen. Separation by glc (A,  $50^\circ$ , 15; 6.3 g passed) gave:- (i) decafluorobicyclo(3,2,0)hept-6-ene(III) nc (2.2 g), b.p.  $71-72^\circ$  (Found: C, 31.6; F, 69.4.  $\text{C}_7\text{F}_{10}$  requires C, 30.7; F, 69.3); ir 1780 (s); m/e 274 (M);  $^{19}\text{F}$ , nmr complex peaks centred at 112 and 176, and two AB groups between 109 and 133 (intensity ratio 1:1:2:1); (ii) 1,3-diene(II) (1.9 g). There was another small peak shown by analytical glc corresponding to the 1,4-diene(I).

Replacement of sodium fluoride as tube packing by iron gauze gave slightly higher conversions. Iron oxide at  $300^\circ$  gave largely unchanged II (containing traces of I and III) in 77% recovery.

(b) The 1,4-Diene(I) Reacted over pellets as above, I (4.9 g) afforded product (3.5 g), separated into III (0.5 g), I (1.7 g), and II (0.2 g), all identified by glc and ir.

When the tube was packed with coarse sodium fluoride powder, the product separated by glc (A,  $50^\circ$ , 13; 4.0 g passed) gave III (1.0 g), I (0.3 g) and II (1.4 g). Passage of I over iron oxide at  $300^\circ$  gave a 75% recovery containing III (trace), I (45%), and II (55%).

(c) Decafluorobicyclo(3,2,0)hept-6-ene(III) and Heated Sodium Fluoride. Reaction as above over sodium fluoride pellets gave 64% recovery comprising III (50%), I (ca 4%), and II (46%).

Passage over glass helices gave 65% recovery, consisting of III (55%), I (trace), II (45%).

Photoisomerisation of the 1,3-Diene(II). Under an atmosphere of nitrogen in a quartz flask, diene II (3.0 g) was irradiated with ultraviolet light for 1 week at  $15^\circ$ . The product (2.5 g) was shown by glc and ir to contain only the decafluorobicyclo-ene(III).

Oxidation of the Decafluorobicyclo-ene(III). III (5.0 g) was added slowly to a stirred solution of potassium permanganate (9.0 g) in water (300 cm<sup>3</sup>) and concentrated sulphuric acid (25 cm<sup>3</sup>), kept at 16°. After 5 h further, sulphur dioxide was passed until the solution was clear and it was then extracted continuously with ether. Evaporation of the ether solution left a syrup (IV) (5.2 g): <sup>19</sup>F nmr, 115-123 (two groups of peaks), 175, in the ratio 2:1:1.

Treatment of the syrup with S-benzylthiuronium chloride gave bis-S-benzylthiuronium octafluorocyclopentane cis-1,2-dicarboxylate(IVa) nc (51% from water), m.p. 124-125° (from water) (Found: C, 43.7; H, 3.7. C<sub>23</sub>H<sub>22</sub>F<sub>8</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub> requires C, 43.5; H, 3.5%), shown by ir to be different from the salt from hexafluoroglutaric acid.

All attempts at decarboxylation of the free acid failed.

Fluorination of the Decafluorobicyclo-ene(III). III (1.3 g) was passed over cobaltic fluoride in a small stirred reactor at 160°. The product was washed and dried to give dodecafluorobicyclo(3,2,0)heptane(V) nc (0.9 g) m.p. ca 22°; m/e 293 (M-F); <sup>19</sup>F nmr, 118-141 (3 groups of peaks), 201, ratio 2:2:1:1.

Reaction of the Decafluorobicyclo-ene(III) with Sodium Borohydride. A suspension of sodium borohydride (1.8 g) in dried diglyme (50 cm<sup>3</sup>) was added dropwise to well-stirred III (6.0 g) in diglyme (40 cm<sup>3</sup>) at -40°. The reaction mixture was allowed to warm up to 0°, and water (100 cm<sup>3</sup>) was then added cautiously. The fluorocarbon layer was well washed with water and dried (2.9 g). Glc (A, 70°, 12) gave:- (i) a mixture (0.2 g): (ii) 6H,7H-octafluorobicyclo(3,2,0)hept-6-ene(VI) nc (1.5 g), m.p. 58° (Found: C, 35.2; H, 1.1. C<sub>7</sub>H<sub>2</sub>F<sub>8</sub> requires C, 35.3; H, 0.8%); ir 1745 (w); m/e 238 (M); nmr, <sup>1</sup>H 3.3 (c); <sup>19</sup>F, 108-135 (two groups of peaks), 176, ratio 1:2:1.

Sodium borohydride (0.35 g) in dry diglyme (30 cm<sup>3</sup>) was added to well-stirred III (2.5 g) in diglyme (15 cm<sup>3</sup>) at -40°. The mixture was worked up immediately and separated by glc (E, 70°, 3.2) to give:- (i) III (trace): (ii) 6H-nonafluorobicyclo(3,2,0)hept-6-ene(VII) nc (0.2 g), m.p. ca 15°, m/e 256 (M); ir, 1680 (s), 3200 (w): (iii) VI (0.2 g).

6-Methoxynonafluorobicyclo(3,2,0)hept-6-ene(VIII). Dry methanol (1.7 cm<sup>3</sup>) was added dropwise to a stirred mixture of III (9.5 g) and potassium hydroxide (2.3 g) at 15°. Heat developed and after further stirring for 20 min. at 15°, water (50 cm<sup>3</sup>) was added. The lower layer was separated,

washed, dried ( $\text{MgSO}_4$ ), and separated by glc (A,  $75^\circ$ , 12; 7.5 g passed) to give:- (i) III (1.5 g); (ii) the 6-methoxyhept-6-ene(VIII) nc (3.4 g) b.p.  $135-136^\circ$  (Found: C, 33.3; H, 1.1.  $\text{C}_8\text{H}_3\text{F}_9\text{O}$  requires C, 33.6; H, 1.1%); m/e 286 (M); ir 2860, 2960 (w) 1745 (s); nmr;  $^1\text{H}$ , 5.9 (d)  $J=1.7$ ;  $^{19}\text{F}$ , 119-145 (three groups of peaks) 131.5, 186.7, 192.6, ratio 2:2:2:1:1:1 : (iii) mixture (0.9 g).

Reaction of the 1,3-Diene(II) with Ethylene. II (23.0 g) and hydroquinone (0.1 g) were sealed in a rocking autoclave in an atmosphere of ethylene (90 atm). After 6 h at  $250-275^\circ$  the autoclave was cooled. Unreacted II (1.3 g) was distilled from the product, leaving a solid (22.5 g) which was sublimed at  $80^\circ/0.5$  mm to give 6H,6H,7H,7H-decafluorobicyclo(3,2,2)non-8-ene(IX) (16.2 g) m.p.  $102^\circ$  (Found: C, 35.9; H, 1.6; F, 62.7.  $\text{C}_9\text{H}_4\text{F}_{10}$  requires C, 35.8; H, 1.3; F, 62.9%); m/e 302 (M); ir 1750 (m); nmr  $^1\text{H}$ , 7.7 (c);  $^{19}\text{F}$ , 115-136 (2 groups of peaks), 147.5, 187, ratio 2:1:1:1.

Oxidation of Adduct IX - IX (2.0 g) with permanganate in acetone in the usual way [8] gave crude 1,2,2,3,3,4,4,5-octafluorocycloheptane-1,5-cis-dicarboxylic acid(X) (2.1 g), as a sticky glass;  $^{19}\text{F}$  nmr, 111-127 (2 AB quartets), 162, in the ratio 2:1:1. The bis-S-benzylthiuronium salt(Xa) nc (58% from water) had m.p.  $195-196^\circ$  (Found: C, 44.9; H, 4.0.  $\text{C}_{25}\text{H}_{26}\text{F}_8\text{N}_4\text{O}_4\text{S}_2$  requires C, 45.3; H, 4.0%).

Fluorination of the Bicyclo-ene(IX). Adduct IX (5.0 g) was vapourised in a nitrogen stream and passed during 45 min into a small stirred cobalt fluoride reactor at  $180^\circ$ . The product was passed over sodium fluoride pellets at  $120-130^\circ$  and collected at  $-180^\circ$ . Nitrogen ( $6 \text{ l h}^{-1}$ ) was passed through the reactor for 1 h further. The product (4.3 g) gave by glc (A,  $70^\circ$ , 14):- (i) endo- or exo- 6H-pentadecafluorobicyclo(3,2,2)nonane(XI) nc (2.0 g) m.p.  $111^\circ$  (Found: C, 27.0; H, 0.2.  $\text{C}_9\text{HF}_{15}$  requires C, 27.4; H, 0.3%); m/e 375 (M-F); nmr,  $^1\text{H}$ , 4.5 (bd  $J=48$ );  $^{19}\text{F}$ , 104-124 (six AB groups of peaks) 202, 209, 215 (d) in the ratio 12:1:1:1 : (ii) a mixture (1.2 g): (iii) 6H,6H-tetradecafluorobicyclo(3,2,2)nonane(XII) nc (0.3 g), m.p.  $119^\circ$  (Found: C, 28.7; H, 0.8.  $\text{C}_9\text{H}_2\text{F}_{14}$  requires C, 28.7; H, 0.5%); m/e 356 (M-HF); nmr,  $^1\text{H}$ , 6.8 (c);  $^{19}\text{F}$ , 115-129 (six groups of peaks), 189, 209, in the ratio 12:1:1.

Fraction (ii) was separated further by glc (E,  $50^\circ$ , 3) to give:- (iia) a mixture of a little XI together with a very similar compound (by nmr) probably its exo- or endo- stereoisomer (0.3 g): (iib) XII (0.5 g).

Dehydrofluorination of the 6H-Bicyclononane(XI). XI (2.0 g), potassium hydroxide (10.0 g) and water (15 cm<sup>3</sup>) were shaken together for 24 h at 100° in a sealed hard-glass tube. The product was separated and distilled at 0.1 mm pressure from a little phosphorus pentoxide to give tetradecafluorobicyclo(3,2,2)non-6-ene(XIII) nc (0.9 g), m.p. 81° (Found: C, 28.4. C<sub>9</sub>F<sub>14</sub> requires C, 28.9%) m/e 374 (M); ir 1760 (s); <sup>19</sup>F nmr, 112-130 (five groups of peaks), 146, 211, ratio 5:1:1.

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