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HIGHLY FLUORINATED HETEROCYCLES. PART XVIII. 2-DIFLUOROMETHYL- AND 2-TRIFLUOROMETHYL- HEXA- AND PENTA- FLUORO-OXOLANS

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SUMMARY

2-Methyltetrahydrofuran with potassium tetrafluorocobaltate(III) at 200 °C gave largely 3H, 4H-2-difluoromethyltrifluoro-3-oxolen. Further fluorination of this by cobalt trifluoride at 120–150 °C afforded many of the stereoisomers expected from saturation of the double bond, and from further replacement of one, and of two hydrogens; viz:- four 3H, 4H-2-difluoromethyl- and two 3H, 4H-2-trifluoromethyl- pentafluoro-oxolans; two 3H- and two 4H- 2-difluoromethylhexafluoro-oxolans; two 3H- and two 4H- 2-trifluoromethylhexafluoro-oxolans. The two trans-3, 4-difluoro-adducts of the starting 3-oxolen were the major individual products, followed by the two cis-analogues, which altogether comprised some 63% of the material isolated. These trans-isomers were interconverted by heated aluminium fluoride, and the 4H/3H-stereoisomer reacted with aluminium chloride by exchanging the α-fluorines for chlorines.

INTRODUCTION

Extending our work on polyfluoroheterocycles [1], this report is on the fluorination by cobaltic fluoride of 3H, 4H-2-difluoromethyltrifluoro-3-oxolen (A; see Chart 1), a compound readily accessible [2] via mild fluorination of 2-methyltetrahydrofuran, using potassium tetrafluorocobaltate [III]. The

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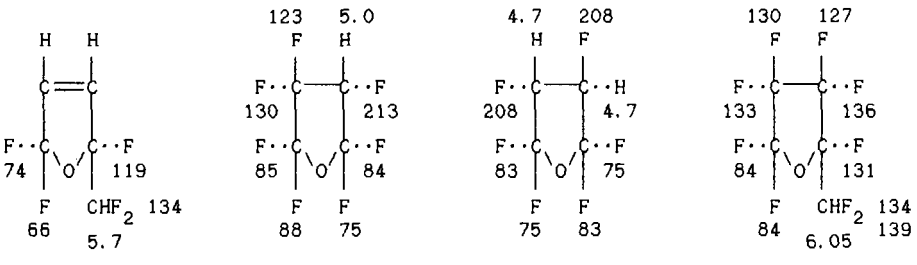
latter reaction gave a crude product containing over 90% of oxolen (A), and this was used directly in the present work. The fluorination of tetrahydrofuran itself was studied earlier [3], and the stereochemistry of the fluorooxolan products was established by relating the ^{19}F nmr peaks to the structural features present (see Chart 1 and Table 1 for the significant data for relevant compounds). The new products now obtained were characterized by extending this approach, in conjunction with other analytical results.

CHART 1

Structures and nmr peak positions for related compounds*



RESULTS

Starting material (A) was fluorinated over cobaltic fluoride at 120-150 °C. A mixture of fifteen components was obtained, of which eleven were isolated pure, by fractional distillation, followed by gas chromatography (see Table 3). Thus, ten new products resulted (I, III-V, VII-X, XII and XIII: see Table 4' and Chart 2). In two cases of closely-related pairs of components (IIa and IIb: VIa and VIb), neither of the mixtures could be separated. Component (XI) was shown to be unreacted starting oxolen (A). Gas chromatographic analyses indicated that four compounds made up ≈63% of the product mixture (IX, 27%; X, 17%; XII, 13%; XIII, 6%). Apart from A (11%), no other one exceeded more than 5% of the total (Table 4).

Elemental analysis of the twelve individual products (see Table 5) divided them into three groups:- (a), (I-III) formulae C_5HF_9O; (b), (IV-VIII)

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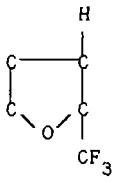
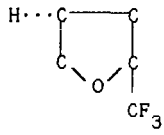
* In Charts 1-3, bonds on opposite sides of ring planes are drawn as vertical solid lines for one side, and horizontal dotted lines for the other.

' In the compound names, substituents on opposite sides of the ring plane are segregated by the symbol / (cf [5]).

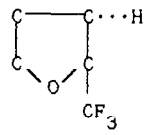
CHART 2



I



IIa



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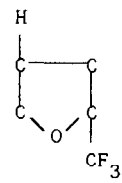
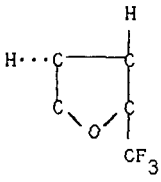


III



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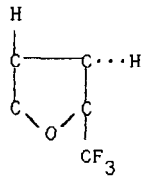

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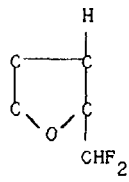
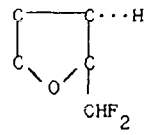
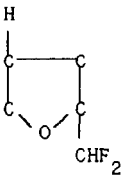


VIa



VIb



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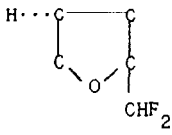
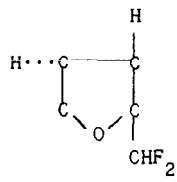


VIII



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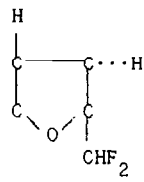
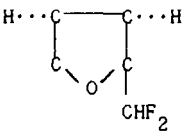


X



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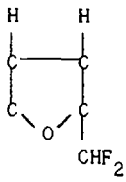
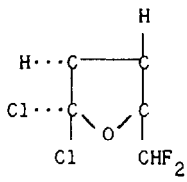
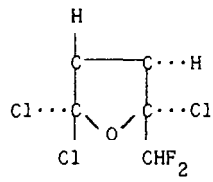


XIII



XIV



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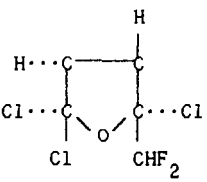
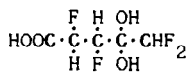


XVI



XVII

All unmarked bonds are to fluorine

formulae $C_5H_2F_8O$; (c), (IX, X, XII, XIII) formulae $C_5H_3F_7O$. The infrared spectra confirmed the absence of olefinic groups (except for XI). Useful information arose from mass spectrometry (see Table 6). Products I-VIII had base peaks at 113 (C_3HF_4). Those with formulae C_5HF_9O had significant peaks for M-F, M-CF_3, C_3HF_5, C_2HF_3, and CF_3. Products of formula $C_5H_2F_8O$ could be divided into two categories: for IV and V, peaks for M-CF_3, $C_3H_2F_3$, $C_2H_2F_2$ and CF_3 were present, but not for M-CHF_2, C_2HF_3 or CHF_2: for VI-VIII, peaks for M-CHF_2, C_3HF_5, C_2HF_3 and CHF_2 were represented, but not those for M-CF_3, $C_2H_2F_2$, or a major one for CF_3. For products of formula $C_5H_3F_7O$, the base peak was at 95 ($C_3H_2F_3$); fragments were found for M-F, M-CHF_2, $C_2H_2F_2$ and CHF_2; but not for CF_3, or for loss of it.

It seemed likely therefore, that the major products (IX, X, XII, XIII) arose by addition of fluorine to the double bond of (A), progressive replacement of hydrogen then following to give the minor products, the skeleton of the starting material (A) being retained throughout. These gross structural allocations were confirmed, and the stereochemical details of the compounds established, from their ^{19}F and ^1H nmr spectra (see Table 7 for details and for reference compounds used, conventions, etc).

Structural allocations from the nmr spectra

Chemical shift values established earlier for groups in polyfluoro-oxolans are given in Chart 1, and couplings present that are of particular significance to the present investigation are listed in Table 1.

TABLE 1

NMR couplings present in compounds A-D

Measurements were carried out as recorded in Table 7

Compound	Positions in ring (Oxygen is 1)			
	2	3	4	5
A [2]	$-CF_2H$; d, J_{HF} = 54 $-CF\cdot CHF_2$; cm $-CH\,F_2$; t, J_{HF} = 54	-	-	AB, J_{AB} = 158
B [3]	AB, J_{AB} = 143	d, J_{HF} = 49.5	AB, J_{AB} = 259	AB, J_{AB} = 137
C [3]	AB, J_{AB} = 145	c	c	AB, J_{AB} = 145
D [4]	$-CF_2H$; dAB, J_{HF} = 51, J_{AB} = 310 $-CF\cdot CHF_2$; m $-CH\,F_2$; td, J_{HF} = 51 J_d = 6.3	AB, J_{AB} = 249	AB, J_{AB} = 253	s

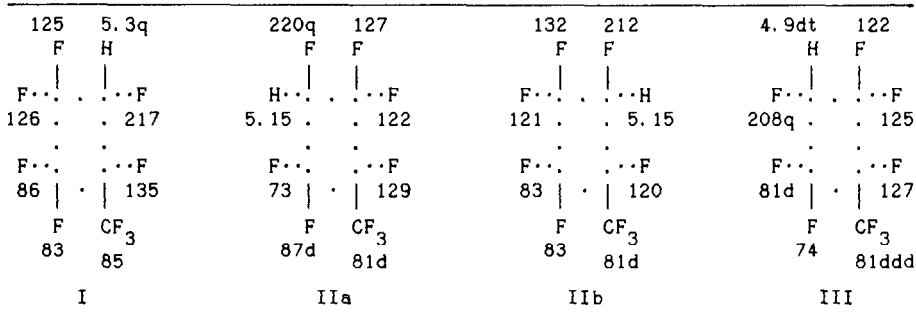
The chemical shift values now found for the new compounds (I-XIV; Table 7) were those expected to arise from the functions whose presence was indicated by mass spectrometry. Thus, ^{19}F peaks were found for $>CF_2$ groups of two types, not adjacent to oxygen [cf 6], and also adjacent to oxygen [3]; however, only >CHF groups not adjacent to oxygen [cf 6,3], were detected. Oxolans I-V showed peaks derived from $-CF_3$ groups, at slightly higher field than for carbocycles [6-8], whilst VI-XII had characteristic peaks for $-CHF_2$, at values similar to those found [7,8] for carbocycles. Peaks for tertiary F were present, but at much lower values than for carbocyclic systems [7,8].

Stereochemical assignments giving the 'best fit' for all the data are listed in Chart 3. Their basis was that chemical shift values were lower for (a) a tertiary fluorine (position 2) when it was cis to a hydrogen on position 3; and for (b) a difluoromethylene fluorine on position 5, when it was cis to a hydrogen on position 4. Also, the doublet from a $-CHF_2$ group was split into an AB system when there was a fluorine cis to it at position 3.

CHART 3

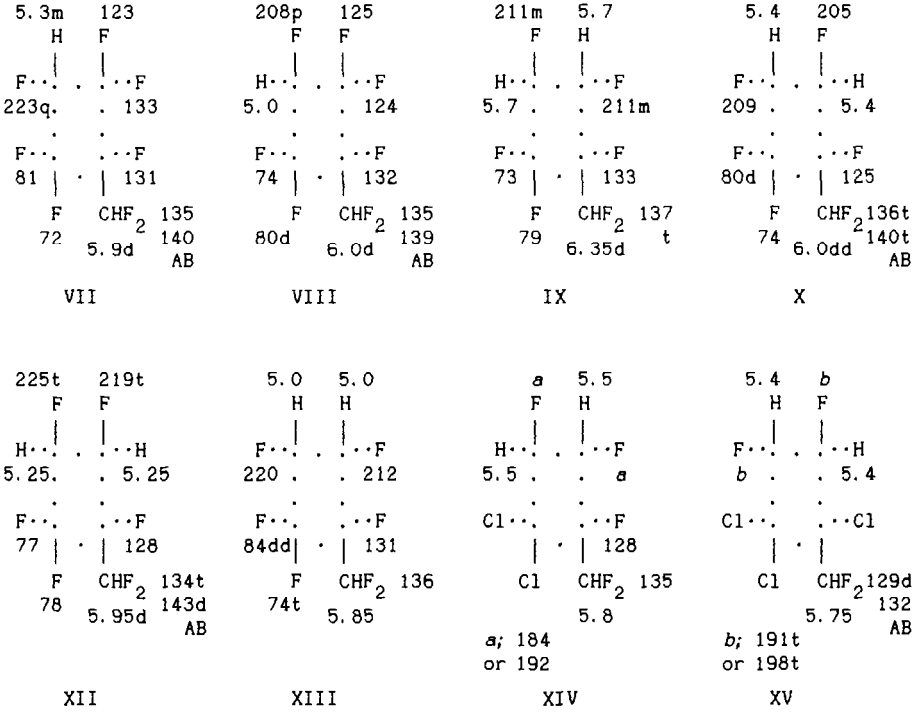
Allocations of nmr peak chemical shifts for compounds I-XVI

Major couplings which are present in all of the compounds are not listed on the formulae, but are summarized below, and are given in detail in Table 7.



(continued)

CHART 3 (cont.)



Couplings present uniformly (not listed above) are:-

$-CHF_2$: H, t; F, d; J_{HF} = 50-60

>CHF : H, d; F, d; J_{HF} = 45-60

$>CF_2$: in positions 3 or 4: AB; J_{AB} = 240-270

$>CF_2$: in position 5: AB; J_{AB} = 135-150

Other couplings present are indicated alongside the chemical shift values on the formulae above.
Many minor unresolved couplings were present also.

The structures given above lead to the minimum number of ambiguities in the peak allocations (Table 7). Furthermore, the ranges of chemical shifts, exhibited by the various types of fluorine, parallel quite closely those in the polyfluoro-oxolan series [3] (Table 2).

TABLE 2

Comparison of ^{19}F nmr chemical shifts

Type of Fluorine	Position[a]	No cis Hydrogen[b]		One cis Hydrogen[b]	
		Fluoro-oxolans[3]	CHF_2- ; CF_3-oxolans	Fluoro-oxolans[3]	CHF_2- ; CF_3-oxolans
$>CF_2$	3	125-141	125-133	123-130	122-124
$>CF_2$	4	125-141	126-132	123-130	121-125
$>CF_2$	5	79-88	78-87	71-76	72-77
>CHF	3	213-226	212-219	206-220	205-211
>CHF	4	213-226	208-225	206-220	208-211

[a] Numbered as in this paper [b] Numbers are ^{19}F chemical shifts.

A fully satisfactory fit for each individual nmr peak is not found in all cases. The >CHF fluorines, at position 4, of compounds III and VIII show rather low-field signals; low enough to suggest that both of them could have hydrogens in the 3 or 5 positions, when clearly they do not. These anomalies are, in fact, paralleled by the case of 2H,4H/-hexafluoro-oxolan [9], which has stereochemistry similar to those of III and VIII (if CF_3 and CHF_2 can be equated with H). It also shows an abnormally low-field signal (206 ppm) for its 4-fluorine. The comments made in our earlier paper [3] about the effects of rapidly equilibrating conformations on the ^{19}F chemical shifts of certain polyfluoro-oxolans obviously also apply to related compounds described here.

There must also be doubts about the mixtures, (II and VI), particularly II, where almost equal proportions of IIa and IIb were present: the structures (Charts 2 and 3) are almost certainly correct, but some of the ^{19}F nmr peak allocations may not be.

Finally, we claim that over the whole range of compounds the structures are the best that can be deduced from the existing data. Interchanging of two isomer allocations, (e.g. IIa with III: IV or V with one of the missing 3H,4H,2-trifluoromethylpentafluoro-oxolans) would lead to further breaches of consistency in the assignments of the ^{19}F nmr spectra, much more profound than those arising from the structures presented in Charts 2 and 3.

Considering the 3H,4H-2-difluoromethylpentafluoro-oxolans (IX, X, XII, XIII), the major individual products, it may be noted that, for related families of compounds, stereoisomers with two cis-hydrogens on adjacent carbons normally have higher boiling points and glc retention times than those with trans [3,5,10]. Further, additions of fluorine to double bonds in cyclic polyfluoride systems usually give more products arising from trans-additions than from cis [7,8,10-12].

OTHER REACTIONS

Polyfluorides are isomerized or dehydrofluorinated by heated aluminium fluoride [3, 13]. Accordingly, 4H/3H, 2-difluoromethylpentafluoro-oxolan (IX) was passed through a heated glass tube packed with AlF_3. There was no effect at 280 °C, but, at 420 °C, mixtures containing IX and low proportions of the stereoisomer X were obtained, and X likewise gave low conversions to IX. Attempts to isomerize compounds IV and V failed, even at 500 °C. Above these respective temperatures, much decomposition occurred. No direct evidence was found for the formation of any polyfluorofurans by dehydrofluorination, but recoveries were poor, and much black solid accumulated in the reaction tube. It is known [14] that polyfluorofurans polymerize spontaneously.

Aluminium trichloride will effect exchange of chlorine for fluorine at the α-CF_2 groups of perfluoro-ethers including oxolans [15]. When the 4H/3H-compound (IX), in methylene chloride, was treated with $AlCl_3$, three products were obtained, again identified by nmr, supplemented by mass spectrometry:- (i), a minor one, 4H/3H, 2-difluoromethyl-5, 5-dichlorotrifluoro-oxolan (XIV); (ii), the major one, 3H/4H, 2-difluoromethyl-2, 5, 5-trichloro-difluoro-oxolan (XV); (iii), the 4H/3H-stereoisomer (XVI) of structure XV (see Chart 2). Appropriate mass spectrometric peaks were present for each, and, in the nmr spectra (see Table 7 and Chart 3), similar features to some of those arising from compounds IX and X were noted, suggesting the structures given above.

Hydrolysis of a mixture of compounds XV and XVI, using oleum at 100 °C, gave an acid (XVII) after an aqueous work-up procedure. Elemental analysis [also that of the anilinium salt (XVIII)], gave a formula $C_5H_6F_4O_4$ for XVII. Nmr and ir spectroscopy showed the presence of two >CHF groups, of one $-CHF_2$ and of hydroxyl functions. Hence, acid XVII had the structure (dl)-threo-2, 3, 5, 5-tetrafluoro-4, 4-dihydroxypent-1-enoic acid, detailed stereochemistry being assumed to be the same as for its precursors (IX and XV/XVI).

The obvious pathway for this hydrolysis is attack by oleum at a carbon-chlorine bond of XV or XVI, forming some type of sulphate ester function; if this occurred at the 2-position, a sulphated cyclic hemi-ketal would result. Any intermediate of this type, from attack at positions 2 or 5, on treatment with water (during work-up) would hydrolyse readily to give the acid (XVII).

EXPERIMENTAL

Fluorination of 2-Methyloxolan by Potassium Tetrafluorocobaltate(III)

Commercial 2-methyltetrahydrofuran (100 g) was passed, as before [2], through a standard stirred reactor [7] (1.2m x 15cm i.d.; 6 Kg $KCoF_4$) at 200 °C, during 3 hours. The reactor was purged with nitrogen (15 lh^{-1} for 1.5 h, and the trap contents were washed well with water. The dried product (≈150 g) was largely 3H, 4H, 2-difluoromethyltrifluoro-3, 4-oxolen (A).

Fluorination of Impure 3H, 4H, 2-Difluoromethyltrifluoro-3, 4-oxolen (A) by Cobalt Trifluoride

Crude product (140 g), made as above, was passed via a liquid seal into a similar reactor (1.3m x 18cm i.d.; packed with 10 Kg of CoF_3) during 3 h. Precise temperature control was difficult; the usual ranges were 120-150 °C. Following a nitrogen sweep (25 lh^{-1} for 2 h) the contents of the cold trap (-78 °C) were poured onto ice and washed well with water (recovery ≈125 g).

Combined products (864 g) were washed (aqueous sodium bicarbonate then water) and dried ($MgSO_4$ then P_2O_5). A part (550 g) was fractionally distilled through a 1m vacuum-jacketed spinning band column, with analysis by glc. Fractions obtained were further separated by preparative glc (Pye Series 104 machine, with a flame-ionization detector; tube packings, Ucon L.B. 550X on Chromasorb P 30-60 (1:4); analysis tube, 1.7m x 4mm i.d.; semi-preparative tube, 9.1m x 7mm i.d.) to give a pure sample of each product, as detailed in Table 3. Glc separation figures are amounts used (cm^3) and column temperatures (°C), respectively; nitrogen flow-rates were 3 lh^{-1}. Proportions of the individual products (Table 4) were based on the glc analysis data.

Isomerization of the 4H/3H- and the 3H/4H-Difluoromethylpentafluoro-oxolans

The apparatus used was an electrically-heated hard glass tube (320mm x 25mm i.d.), packed with a 1:1 mixture (ca 300 g) of aluminium fluoride and small glass spheres. Before use, this was heated to 280 °C for 24 h, whilst a slow stream of nitrogen was passed through.

With the tube temperature at 420 °C, 4H/3H, 2-difluoromethylpentafluoro-oxolan (IX; 3.0g) was passed through during 30 min. in a stream of nitrogen (1 lh^{-1}). The product (2.15 g) had two components, and glc separation (0.5 g), as before, afforded:- (i) recovered IX (0.28 g); (ii) the 3H/4H-stereoisomer (X; 0.02 g); identified spectroscopically.

From compound X, treated similarly, there were obtained:- (i) isomer IX (0.02 g); (ii) recovered X (0.30 g).

Even at temperatures up to 500 °C, the trifluoromethyl compounds IV and V did not isomerize. In each case, only the starting material was recovered.

TABLE 3

Isolation of the products of fluorination

Fraction No.	Wt (g)	Boiling range (°C)	Glc separations		Sub-fraction No.	Compound No.	Wt (g)
1	22.4	26-46	2.5	60	(i)	I	1.2
					(ii)	II	1.1
2	7.8	46-48	-		-	-	-
3	10.9	48-53	3.5	80	(i)	III	0.8
					(ii)	IV	1.9
4	14.2	53-54	-		-	mainly IV	
5	16.2	54-64	2.6	100	(i)	IV	0.8
					(ii)	V	0.8
					(iii)	VI	0.6
6	15.8	64-69	-		-	-	-
7	15.7	69-71.5	-		-	-	-
8	35.7	71.5-78	-		-	-	-
9	19.7	78-81	2.3	100	(i)	VII	0.6
					(ii)	VIII	0.4
					(iii)	IX	1.0
10	14.1	81-82	-		-	mainly IX	
11	34.8	82	-		-	IX	34.8
12	25.3	82	-		-	mainly IX	
13	55.2	82-85	-		-	-	-
14	55.4	85-90	2.5	118	(i)	IX	1.2
					(ii)	X	1.1
15	17.2	90	-		-	X	17.2
16	13.5	90-92	-		-	mainly X	
17	12.0	92	-		-	-	-
18	28.5	92-94	-		-	-	-
19	18.1	94-98	-		-	-	-
20	30.6	98-107	2.0	130	(i)	X	0.9
					(ii)	XI	1.0
21	11.2	107-110	-		-	-	-
22	17.6	110-112	2.0	130	(i)	XII	1.0
					(ii)	XIII	0.7
23	9.3	112-118	-		-	-	-
24	13.3	Still residue	-		-	-	-

TABLE 4

List of individual products isolated (all are new compounds)

Number	Name of Compound	Present in Fraction	Amount (%)*
I	3H, 2-trifluoromethylhexafluoro-oxolan	1	1
IIa}	{ 3H/2-trifluoromethylhexafluoro-oxolan }	1, 2	1.5
IIb}	{ 4H/2-trifluoromethylhexafluoro-oxolan }	1, 2	1.5
III	4H, 2-trifluoromethylhexafluoro-oxolan	2, 3	0.5
IV	4H/3H, 2-trifluoromethylpentafluoro-oxolan	3-5	4.5
V	3H/4H, 2-trifluoromethylpentafluoro-oxolan	5, 6	4
VIa}	{ 3H, 2-difluoromethylhexafluoro-oxolan }	5-7	3.5
VIb}	{ 3H/2-difluoromethylhexafluoro-oxolan }	5-7	2.5
VII	4H, 2-difluoromethylhexafluoro-oxolan	6-9	4.5
VIII	4H/2-difluoromethylhexafluoro-oxolan	7-9	3.5
IX	4H/3H, 2-difluoromethylpentafluoro-oxolan	9-14	27
X	3H/4H, 2-difluoromethylpentafluoro-oxolan	14-20	17
XII	3H, 4H/2-difluoromethylpentafluoro-oxolan	21, 22	13
XIII	3H, 4H, 2-difluoromethylpentafluoro-oxolan	22-24	6
XI - Identical spectroscopically to starting material A		19-21	11

*Approximate values only, and volatile products may be over-estimated by glc

TABLE 5

Boiling points and elemental analyses of compounds I-X, XII, XIII

No.	Boiling Point (°C)	Formula	Required (%) C	H	F	Found (%) C	H	F
I	42-43	C_5HF_9O	-	-	-	-	-	-
II	≈45	C_5HF_9O	24.2	0.4	68.9	23.9	0.4	-
III	48.5	C_5HF_9O	24.2	0.4	68.9	24.2	0.5	69.5
IV	54	$C_5H_2F_8O$	26.1	0.9	66.1	25.9	0.7	65.4
V	61	$C_5H_2F_8O$	26.1	0.9	66.1	26.1	0.9	66.1
VI	67-68	$C_5H_2F_8O$	26.1	0.9	66.1	26.1	1.0	66.0
VII	71-72	$C_5H_2F_8O$	26.1	0.9	66.1	26.0	0.9	66.1
VIII	74-75	$C_5H_2F_8O$	26.1	0.9	66.1	26.1	1.0	66.6
IX	81	$C_5H_3F_7O$	28.3	1.4	62.7	28.3	1.4	63.3
X	90	$C_5H_3F_7O$	28.3	1.4	62.7	28.0	1.4	62.9
XII	107-108	$C_5H_3F_7O$	28.3	1.4	62.7	28.6	1.6	62.3
XIII	112	$C_5H_3F_7O$	28.3	1.4	62.7	28.3	1.4	62.4

TABLE 6

Major mass spectrometric peaks (measured on an A.E.I. MS9 instrument)

+ significant peak present: ++ base peak: - peak absent

	M-F (229)	M-F-HF (209)	M-CF_3 (179)	C_3HF_6 (151)	C_3HF_5 (132)	C_3F_5 (131)	C_3HF_4 (113)	C_2F_4 (100)	C_2HF_3 (82)	CF_3 (69)
M = C_5HF_9O (compound nos. I - III; II is a mixture of IIa + IIb)										
I	+	+	+	+	+	+	++	-	+	+
II	+	+	+	+	+	+	++	+	+	+
III	+	+	+	+	+	+	++	-	+	+

	M-F (211)	M-CHF_2 (179)	M-CF_3 (161)	C_3HF_6 (151)	$C_3H_2F_5$ (133)	C_3HF_5 (132)	C_3HF_4 (113)	$C_3H_2F_3$ (95)	C_2HF_3 (82)	$C_2H_2F_2$ (64)	CHF_2 (51)
M = $C_5H_2F_8O$ (compound nos. IV - VIII; VI is a mixture of VIa and VIb)											
IV	-	-	+	-	+	-	++	+	-	+	-
also at 145 (M-CF_3O) and 69 (CF_3)											
V	+	-	+	-	+	-	++	+	-	+	-
also at 69 (CF_3)											
VI	+	+	-	+	-	+	++	+	+	-	+
VII	+	+	-	+	-	+	++	+	+	-	+
also at 191 (M-F-HF)											
VIII	+	+	-	+	-	+	++	+	+	-	+
also at 191 (M-F-HF)											

	M-F (193)	M-CHF_2 (161)	M-CHF_2O (145)	$C_3H_2F_5$ (133)	C_3HF_4 (113)	$C_3H_2F_3$ (95)	$C_2H_2F_2$ (64)	CHF_2 (51)
M = $C_5H_3F_7O$ (compound nos. IX, X, XII and XIII)								
IX	+	+	+	+	+	++	+	+
X	+	+	+	+	+	++	+	+
XII	-	+	+	+	+	++	+	+
XIII	+	+	+	+	+	++	+	+

Reaction of the 4H/3H,2-Difluoromethyl-oxolan (IX) with Aluminium Chloride

4H/3H,2-difluoromethylpentafluoro-oxolan (5.0 g), freshly-sublimed aluminium chloride (3.0 g) and methylene chloride (5 cm^3) were stirred together at 15 °C, a dark orange colour developing. The solid residue was filtered off and washed with methylene chloride. The combined solvents were dried and concentrated to leave a liquid (1.1 g). This was separated by glc (tube packing, 1:6 polyethylene glycol adipate on Chromasorb P; temp. 140 °C; flow rate 4.5 lh^{-1}) to give four fractions:- (i) methylene chloride: (ii) 4H/3H, 2-difluoromethyl-5,5-dichlorotrifluoro-oxolan (XIV) (nc) (0.09 g); MS peaks

TABLE 7

Nmr spectral peaks (measured on a Perkin-Elmer R10 spectrometer)

^1H shifts (60 MHz) are listed in p.p.m. to low field of tetramethylsilane, ^{19}F shifts (56.4 MHz) to high field of trichlorofluoromethane, both internal standards. AB signal positions are given by $\delta \upsilon/2$ from the centre; other signals: - b, broad: c, complex; d, doublet; m, multiplet; p, pentet; q, quartet; s, singlet; t, triplet. The solvent was carbon tetrachloride.

Compound Number		Chemical Shifts	Relative Intensity		Position in Formula	Type of Signal and Couplings
I	H	5.3	-		>CHF	dq; J_{HF} = 48
	F	83.3; 85.9	2		5, $>CF_2$	AB; J_{AB} = 136
		85.2	3		$-CF_3$	s
		125.0; 125.6	2		4, $>CF_2$	AB; J_{AB} = 244
		135.4	1		$>CF\cdot CF_3$	c
		217.3	1		>CFH	d; J_{HF} = 50
(II)	H	5.15	-		>CHF	d; J_{HF} = 48
IIa	F	72.6; 87.4	-	IIa	5, $>CF_2$	ABd; J_{AB} = 136
+ IIb		82.7; 83.4	-	IIb	5, $>CF_2$	AB; $J_{AB} \approx 140$
IIa + IIb	F	81.0	-	IIa	$-CF_3$	d
		81.4	-	IIb	$-CF_3$	d
		120.0	-	IIb	$>CF\cdot CF_3$	s
		121.5; 127.3	-	IIa	3, $>CF_2$	AB; $J_{AB} \approx 280$
		121.1; 131.9	-	IIb	4, $>CF_2$	AB; $J_{AB} \approx 265$
		129.0	-	IIa	$>CF\cdot CF_3$	s
		212.4	-	IIb	>CHF	d; J_{HF} = 51
		220.5	-	IIa	>CHF	dq; J_{HF} = 51
III	H	4.9	-		>CHF	ddt; J_{HF} = 48; J_{HF} = 3; 6
	F	74.2; 81.0	2		5, $>CF_2$	ABd; J_{AB} = 147; J_{FF} = 10
		81.1	3		$-CF_3$	ddd; J_{FF} = 11; 4.5; 2.5
		121.8; 124.6	2		3, $>CF_2$	AB; J_{AB} = 271
		127.3	1		$>CF\cdot CF_3$	m
		208.1	1		>CFH	dq; J_{HF} = 48; $J_{FF} \approx 10$
IV	H	≈ 5.4	-		>CHF	cd; J_{HF} = 50-60
	F	74.2; 79.8	2		5, $>CF_2$	AB; J_{AB} = 136
		85.0	3		$-CF_3$	bs
		133.1	1		$>CF\cdot CF_3$	s
		210.2	1		>CFH	d; J_{HF} = 58
		211.2	1		>CFH	d; J_{HF} = 58

(continued)

TABLE 7 (cont.)

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
V	H	≈ 5.35	–	>CHF	cd; J_{HF} = 45
	F	75.4; 80.5	2	5, $>CF_2$	ABd; J_{AB} = 148
		81.5	3	$-CF_3$	dd
		119.5	1	$>CF\cdot CF_3$	m
		205.7	1	3, >CFH	d; J_{HF} = 49
		208.1	1	4, >CFH	cd; J_{HF} = 50
VIa	H	≈ 5.15	1	>CHF	dm; J_{HF} = 51
		5.90	1	$-CHF_2$	tt; J_{HF} = 54
(VI)	F	83.7; 85.5	2	5, $>CF_2$	AB; J_{AB} = 136
		124.8; 125.6	2	4, $>CF_2$	AB; J_{AB} = 260
		132.7	1	$>CF\cdot CHF_2$	s
		136.3	2	$-CF_2H$	d; J_{HF} = 50
		218.6	1	>CFH	d; J_{HF} = 47
VIb	H	≈ 5.15	1	>CHF	d; J_{HF} = 51
		5.90	1	$-CHF_2$	tt; J_{HF} = 54
(VI)	F	81.3; 87.2	2	5, $>CF_2$	ABd; J_{AB} = 136
		121.0; 131.8	2	4, $>CF_2$	AB; J_{AB} = 260
		127.1	1	$>CF\cdot CHF_2$	s
		134.0; 142.0	2	$-CF_2H$	ABdd; J_{AB}= 320; J_{HF}= 51
		214.2	1	>CFH	d; J_{HF} = 51
VII	H	5.3	1	>CHF	dm; J_{HF} = 45
		5.9	1	$-CHF_2$	td; J_{HF} = 51
	F	72.3; 81.0	2	5, $>CF_2$	AB; J_{AB} = 136
		122.6; 132.8	2	3, $>CF_2$	AB; J_{AB} = 244
		130.8	1	$>CF\cdot CHF_2$	s
		134.6; 139.6	2	$-CF_2H$	ABd; J_{AB}= 310; J_{HF}= 50
		222.7	1	>CFH	dq; J_{HF}= 49
VIII	H	5.0	1	>CHF	cd; J_{HF} = 48
		6.0	1	$-CHF_2$	td; J_{HF} = 51
	F	74.3; 80.3	2	5, $>CF_2$	ABd; J_{AB} = 148
		123.7; 124.7	2	3, $>CF_2$	AB; J_{AB} ≈ 280
		131.8	1	$>CF\cdot CHF_2$	m
		134.9; 139.1	2	$-CF_2H$	ABd; J_{AB}= 310; J_{HF}= 56
		208.5	1	>CFH	dp; J_{HF} = 50

(continued)

TABLE 7 (cont.)

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
IX	H	≈ 5.7	2	2 × >CHF	dm; J_{HF} = 60
		6.35	1	$-CHF_2$	td; J_{HF} = 53
	F	72.85; 79.35	2	5, $>CF_2$	AB; J_{AB} = 148
		132.7	1	$>CF\cdot CHF_2$	s
		136.9	2	$-CF_2H$	dt; J_{HF} = 52
		211.0	1	>CFH	dm; J_{HF} = 50
		211.2	1	>CFH	dm; J_{HF} = 50
X	H	≈ 5.4	2	2 × >CHF	dm; J_{HF} = 48
		6.0	1	$-CHF_2$	tdd; J_{HF} = 53
	F	74.2; 80.4	2	5, $>CF_2$	ABd; J_{AB}= 148; J_d= 10
		124.9	1	$>CF\cdot CHF_2$	m
		135.5; 139.7	2	$-CF_2H$	ABdt; J_{AB}= 306; J_{HF}= 56; J_t= 10
X		205.4	1	>CFH	d; J_{HF} = 49
		209.3	1	>CFH	d; J_{HF} = 49
XII	H	5.25	2	2 × >CHF	cd; J_{HF} = 54
		5.95	1	$-CHF_2$	td; J_{HF} = 51
	F	76.7; 78.2	2	5, $>CF_2$	AB; J_{AB} = 135
		127.7	1	$>CF\cdot CHF_2$	bs
		133.9; 142.6	2	$-CF_2H$	ABtd; J_{AB}= 300; J_{HF}= 50
		218.8	1	>CFH	dt; J_{HF} = 51
		224.8	1	>CFH	dt; J_{HF} = 51
XIII	H	≈ 5.0	2	2 × >CHF	cd; J_{HF} = 51
		5.85	1	$-CHF_2$	t; J_{HF} = 54
	F	73.5; 83.5	2	5, $>CF_2$	ABtdd; J_{AB} = 148
		130.6	1	$>CF\cdot CHF_2$	s
		136.2	2	$-CF_2H$	cd; J_{HF} = 60
		212.1	1	>CFH	d; J_{HF} = 54
		220.5	1	>CFH	d; J_{HF} = 51
XIV	H	≈ 5.5	2	2 × >CHF	d; J_{HF} = 50
		5.8	1	$-CHF_2$	t; J_{HF} = 51
	F	127.6	1	$>CF\cdot CHF_2$	s
		135.5	2	$-CF_2H$	d; J_{HF} = 51
		≈ 184	1	>CFH	c
		≈ 192	1	>CFH	c

(continued)

TABLE 7 (cont.)

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
XV	H	≈ 5.4	2	2 × >CHF	d; J_{HF} = 51
		5.75	1	$-CHF_2$	t, J_{HF} = 54
	F	128.9; 131.9	2	$-CF_2H$	ABdd; J_{AB}= 282; J_{HF}= 53
		190.9	1	>CFH	dt; J_{HF} = 53
		197.6	1	>CFH	dt; J_{HF} = 53
XVI	H	≈ 5.4	2	2 × >CHF	d; J_{HF} = 54
		5.85	1	$-CHF_2$	t; J_{HF} = 54
	F	130.4	2	$-CF_2H$	ddd; J_{HF} = 53
		176.9	1	>CFH	ddd; J_{HF} = 48
		197.8	1	>CFH	m
XVII	Solvent: acetone-d_6				
	H	4.95	1	>CHF	dd; J_{HF} = 45; 27
		5.45	1	>CHF	dd; J_{HF} = 46; 29
		5.8	1	$-CHF_2$	t; J_{HF} = 55
	F	132.1; 139.1	2	$-CF_2H$	ABd; J_{AB} = 284
		208.5	1	>CFH	m
		212.0	1	>CFH	m

at 209 (M-Cl), 193 (M-CHF_2), 146 ($C_4H_3F_5$), 111 ($C_3H_2ClF_2$), 95 ($C_3H_2F_3$; base peak), 67 (CHClF), 63 (CClO), 51 (CHF_2): (iii) 3H/4H,2-difluoromethyl-2,5,5-trichlorodifluoro-oxolan (XV) (nc) (0.70 g); b.p. 166-167 °C; (Found: C, 22.6; H, 1.1; Cl, 40.6; F, 28.7. $C_5H_3Cl_3F_4O$ requires C, 23.0; H, 1.15; Cl, 40.7; F, 29.1%); M/e, 225 (M-Cl), 209 (M-CHF_2), 161 ($C_4H_2ClF_4$), 127 ($C_3H_2Cl_2F$), 111 ($C_3H_2ClF_2$; base), 67, 63, 51: (iv) 4H/3H,2-difluoromethyl-2,5,5-trichlorodifluoro-oxolan (XVI) (nc) (0.20 g); b.p. 171 °C; (Found: C, 23.1; H, 1.1; Cl, 40.4; F, 29.3%); M/e, peaks as for compound (XV) (in this section, only the peaks for ^{35}Cl are recorded; those for ^{37}Cl were present).

2,3,5,5-Tetrafluoro-4,4-dihydroxypent-1-enoic Acid (XVII)

A mixture of 3H/4H- (XV) and 4H/3H,2-difluoromethyl-2,5,5-trichlorodifluoro-oxolan (XVI) (3.0 g) was stirred with oleum (10 cm^3 ; 30% SO_3) for 15 hours at 100 °C. The dark red mixture was cooled, poured onto crushed ice, and the aqueous solution was extracted with ether. The extracts were dried and evaporated to an oil, which crystallized (1.5 g). Two sublimations (100

°C/50 mm Hg) afforded white waxy crystals of (dl)-threo-2,3,5,5-tetrafluoro-4,4-dihydroxypent-1-enoic acid (XVII) (nc) (1.3 g); m.p. 91-92 °C; (Found: C, 29.45; H, 3.1; F, 36.4. $C_5H_6F_4O_4$ requires C, 29.2; H, 2.9; F, 36.9%); ir bands at 3500, 3200b, 1740 cm^{-1}.

Freshly-distilled aniline was added dropwise to acid (XVII) (0.5 g), in dried ether (5 cm^3), until precipitation was complete. Filtration, and washing with ether gave the anillinium salt (XVIII) (nc) (0.4g); m.p. 123 °C (dec.); (Found: C, 44.5; H, 4.7; F, 25.2; N, 4.7. $C_{11}H_{13}F_4NO_4$ requires C, 44.2; H, 4.4; F, 25.4; N, 4.7%); ir band at 3460 cm^{-1} (OH).

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