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HIGHLY FLUORINATED HETEROCYCLES. PART XIX. DEHYDROFLUORINATION STUDIES ON 2-DIFLUOROMETHYL- AND 2-TRIFLUOROMETHYL-HEXA- AND -PENTAFLUORO-OXOLANS

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SUMMARY

The four 3H, 4H-2-difluoromethylpentafluoro-oxolans reacted with powdered potassium hydroxide in suspension in benzene to give 3H- (1) and 4H- (2) 2-difluoromethyltetrafluoro-3, 4-oxolen, different proportions being formed from each stereoisomer. 3H/4H- and 4H/3H-2-Trifluoromethylpentafluoro-oxolans likewise afforded different proportions of 3H- (3) and 4H- (4) 2-trifluoromethyltetrafluoro-3, 4-oxolen. From similar dehydrofluorinations of mixed isomers of 3H- and 4H- 2-difluoromethylhexafluoro-oxolan, there were formed 2-difluoromethylpentafluoro-3, 4- (5) and -2, 3- (6) oxolen; mixed 3H- and 4H-2-trifluoromethylhexafluoro-oxolan afforded an inseparable mixture of 2-trifluoromethylpentafluoro-3, 4- (7a) and -2, 3- (7b) oxolen. With cobaltic fluoride, oxolen (5) gave 2-difluoromethylheptafluoro-oxolan (8). On treatment with aqueous potassium hydroxide, (8) underwent ring-opening, forming tetrafluoropent-2-en-1, 5-dioic acid (10). Diels-Alder adducts resulted from reactions of oxolen (7a) with cyclopentadiene and with furan.

INTRODUCTION

This paper describes dehydrofluorination reactions on some polyfluoro-oxolans, obtained [1] by further fluorination of 3H, 4H-2-difluoromethyltrifluoro-3-oxolen, which was accessible [2] via mild fluorination of 2-methyl-

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tetrahydrofuran. Dehydrofluorinations of polyfluoro-cycloalkanes to -arenes were carried out [3,4] using aqueous potassium hydroxide, but this was not effective for analogous syntheses of tetrafluoro- -furan [5] and -thiophen [6], molten potash being required. For the present oxolans, an anhydrous system [cf 7] seemed preferable , $-CHF_2$ groups being often involved, and KOH in suspension in benzene (to facilitate glc monitoring) at room temperature was the reagent chosen. In two cases , mixtures of a 3,4- and a 2,3-oxolen were formed; the other reactions gave 3,4-oxolens. No furans were found.

RESULTS

The first dehydrofluorination was of 4H/3H,2-difluoromethylpentafluoro-oxolan (IX; see Scheme A *), present in the greatest proportion [1]. The two major products both had correct elemental analyses (Table 3), and consistent ir (Table 2), and mass spectra (Table 4), for hexafluoro-oxolens (formed by losing 1 mol. of HF). By comparison with the earlier data [1], their ^{19}F nmr spectra (Table 5) showed that their structures were 3H- and 4H- 2-difluoromethyltetrafluoro-3,4-oxolen (1 and 2 respectively). Peaks were present for $>CF_2$ (at C-5) and for $-CHF_2$ (chemical shift values were close to those found for such groups in IX itself) and also for a tertiary F and for a vinylic F. The low shift value from the tertiary F of oxolen (1) arose from the proximity of a vinylic H at position 3. For oxolen (2) the values for the $>CF_2$ at C-5 were low because there was a vinylic H alongside at C-4.

These allocations were confirmed chemically. Oxolen (2) was oxidized to 2-difluoromethyltrifluoro-3-oxaglutaric acid (9), characterized as the dianilinium (9a) and as the known [2] bis-S-benzylthiuronium (9b) salts. Passage of oxolen (1) over cobalt trifluoride at 140 °C gave addition to the double bond with minimal replacement of hydrogen, and a mixture of 3H,2- and 3H/2-difluoromethylhexa-fluoro-oxolan (VIa and VIb [1]) was obtained.

The other three 3H,4H,2-difluoromethylpentafluoro-oxolan stereoisomers (X, XII, XIII) were dehydrofluorinated in the same manner, and the same two products (1, 2) were formed (Scheme A), though in different proportions for

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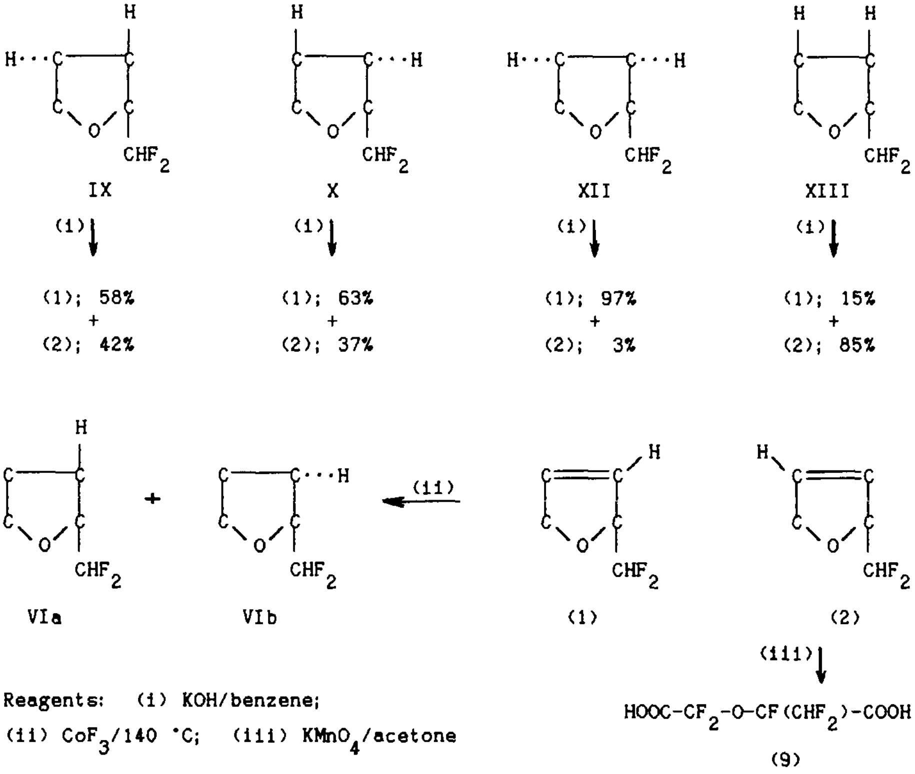
* In this paper, the oxolan precursors are given the same Roman numbers as in Ref [1], where, in the Charts, bonds on opposite sides of ring planes are drawn as vertical solid lines for one side, and, for the other, as horizontal dotted lines. In the compound names, substituents on opposite sides of the ring plane are segregated by the symbol / (cf [3]).



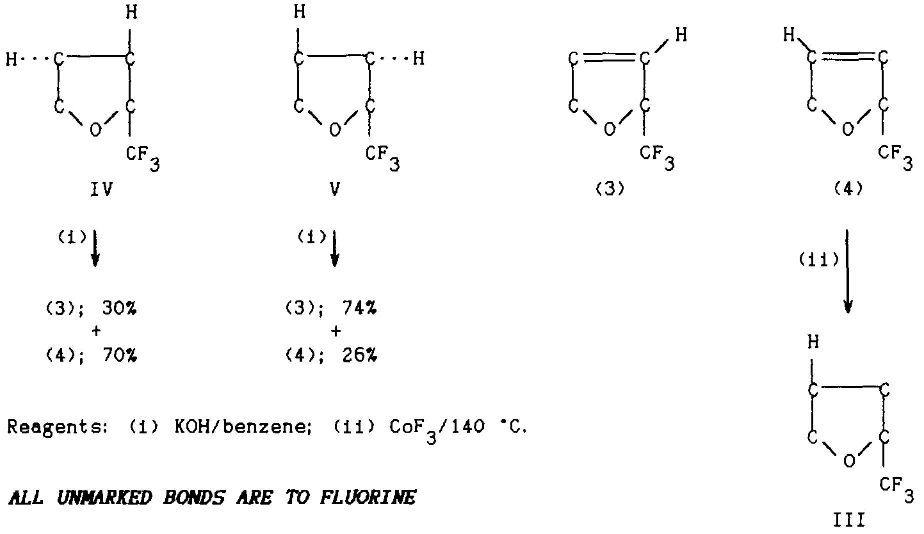
Reagents: (i) KOH/benzene;
(ii) CoF_3/140 °C; (iii) $KMnO_4$/acetone

ALL UNMARKED BONDS ARE TO FLUORINE

SCHEME A

each compound (see the later discussion). In two cases (IX and XIII) traces of two compounds with short glc retention times were detected. Absorptions in their ir spectra indicated unsaturation, and the presence of polyfluorofurans is possible, but this is only conjecture.

Dehydrofluorinations of 4H/3H,2-trifluoromethylpentafluoro-oxolan (IV), carried out similarly, afforded the two analogous oxolens bearing CF_3 groups (3 and 4, respectively; Scheme B). Analytical and spectroscopic data were very similar to those of oxolens (1) and (2), and product (4) was confirmed as the 4H-isomer by reaction with cobalt trifluoride. In this case, only one stereoisomer, 4H,2-trifluoromethylhexafluoro-oxolan (III) was detected among the products, but the other may have been present in a smaller fraction. A parallel dehydrofluorination was done on 3H/4H,2-trifluoromethylhexa-fluoro-



Reagents: (i) KOH/benzene; (ii) CoF_3/140 °C.

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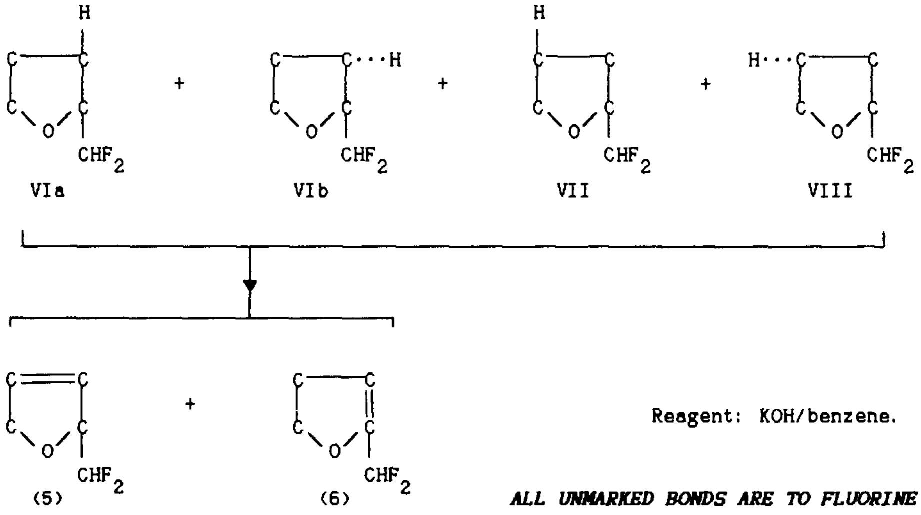
SCHEME B

oxolan (V), the stereoisomer of oxolan (IV) (see Ref [1], Chart 2); the same two oxolens (3 and 4) were obtained, but in different proportions from (IV) than from (V). Again, this aspect is considered in the later discussion.

Separation of pure 3H- and 4H- 2-difluoromethylhexafluoro-oxolans (VIa, VIb, VII, VIII; Chart 2 [1]) was difficult, and so a mixture of all four was subjected to the standard dehydrofluorination process. Two heptafluoro-oxolens were obtained and separated by glc (see Scheme C). That with the lower retention time (5) had a skeleton similar to those of products (1-4), and F in both vinylic positions. There was a peak in the ir at 1800 cm^{-1} and ^{19}F nmr peaks at appropriate positions for all the substituents present. Product (5) was therefore 2-difluoromethylpentafluoro-3,4-oxolen.

The second product (6) was an isomer: the ^{19}F nmr spectrum showed that it retained a difluoromethyl group, but no peak for a tertiary F at C-2 was observed. However, peaks corresponding to two $>CF_2$ groups and to one vinylic F were present; there was a $>C=C<$ band in the ir at 1750 cm^{-1}. These data showed clearly that (6) was 2-difluoromethylpentafluoro-2,3-oxolen.

This isomer must have arisen only from the 3H-oxolans (VIa and VIb); to check whether these gave rise to (6) exclusively, mixed VIa and VIb were dehydrofluorinated similarly. Both oxolens (5 and 6) were in fact formed.



Reagent: KOH/benzene.

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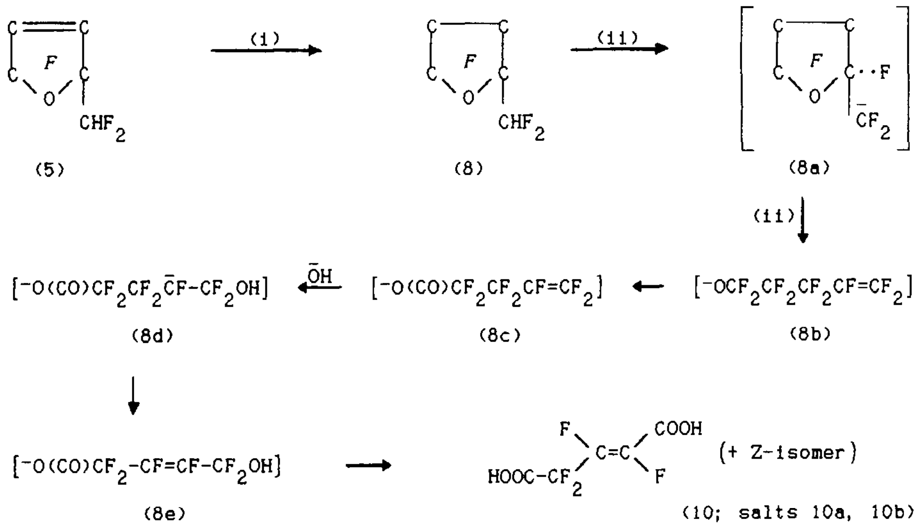
SCHEME C

Passage of oxolen (5) over cobalt trifluoride at 120 °C again effected addition to the double bond with negligible hydrogen replacement, and 2-difluoromethylheptafluoro-oxolan (8) was synthesized (Scheme D). The spectroscopic parameters were those anticipated for this saturated structure.

Compound (8) offered interesting alternatives for reactions with bases. There are possibilities of forming a compound with an exocyclic double bond, or, since these products are not formed readily, of trapping an intermediate carbanion and thereby replacing the H in a synthetically useful manner. The latter technique has been very successful when applied to polyfluorobicyclic species [8]. Accordingly, reaction of oxolan (8) with potassium hydroxide in a medium of dimethyl sulphoxide and water in the presence of formaldehyde was attempted, to try to convert $-CF_2H$ into $-CF_2CH_2OH$. However, the product was not an alcohol but a carboxylic acid (10; Scheme D) and reaction in the absence of formaldehyde, either at 80 or at 0 °C, gave the identical acidic material. Attempts to generate a carbanion from (8) by use of dimsyl sodium (from dimethyl sulphoxide + NaH [9]) were unsuccessful; even at -78 °C, only dark polymeric products were obtained.

Product (10) was identified as tetrafluoropent-2-en-1,5-dioic acid from its dianilinium (10a) and bis-S-benzylthiuronium (10b) salts (correct elemental analyses) and from the ^{19}F nmr spectrum of the crude acid (Table 5).



Reagents: (i) CoF_3/120 °C; (ii) KOH/H_2O/dimethyl sulphoxide

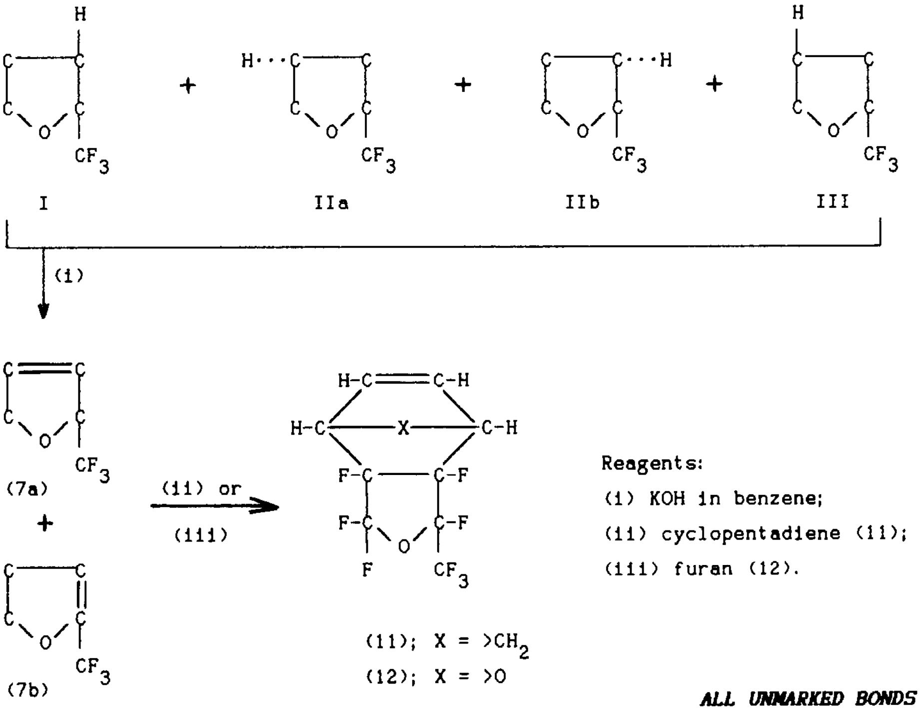
SCHEME D

Acid (10) was a mixture of E and Z isomers in about a 4:1 ratio, as coupling constants of 134 Hz in the major isomer and of 6.9 Hz in the minor one are within the well-established ranges for trans and for cis -CF=CF-, respectively. The dianilinium salt (10a) also appeared to be an analogous mixture of stereoisomers, although the ^{19}F nmr spectrum of the minor component of the salt was too weak to leave us feeling completely sure on this point.

An idealized pathway to acid (10) from the saturated oxolen (8) is summarized in Scheme D. It seems likely that a developing negative charge on the side chain of (8a) feeds into the ring at C-2, but is not transmitted to the tertiary fluorine (ie., an exocyclic alkene is not an intermediate). If it were, the vinylic fluorine at C-2 in acid (10) would arise by a fluorine migration; possible, but less likely. The negative charge of (8a) transfers to oxygen, and ring-opening follows to give (8b). A series of hydrolytic stages similar to those depicted (8b → 8e) will lead to the product (10). A similar ring-opening reaction is found for non-fluorinated oxolans [10].

Consideration of molecular models suggests that the form of intermediate (8d) having an antiperiplanar arrangement of an F on C-3 and the negative charge (best for elimination), and with least steric interactions, would lead to trans -FC=CF- geometry (acid (10) was mainly the E-isomer).

3H and 4H, 2-Trifluoromethylhexafluoro-oxolans (I, IIa, IIb, III) were also dehydrofluorinated as a mixture, since separation was difficult. Two oxolens were formed (7a, 7b; Scheme E), as with the difluoromethyl analogues (VIa, VIb, VII, VIII), but here they could not be separated. They were 2-trifluoromethylpentafluoro-3,4-oxolen (7a), and the isomeric -2,3-oxolen (7b), identified by the ^{19}F nmr spectrum of the mixture, which showed features very similar to those of oxolens (5) and (6). There were peaks in the ir for -C=C- at 1805 (major component) and 1750 cm^{-1} (minor), again resembling those for (5) and (6). The 7a:7b ratio was about 9:1, somewhat greater than the 5:6 ratio (2:1). This cannot be due solely to differences in composition of the starting mixtures, since these were much the same (*ie.*, the relative amounts of VIa, VIb, VII and VIII were not very different from those of I, IIa, IIb and III), and so must be due to chemical factors peculiar to each set of compounds.



Reagents:
(i) KOH in benzene;
(ii) cyclopentadiene (11);
(iii) furan (12).

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SCHEME E

Some cyclo-addition reactions of the oxolen mixture (7) were studied. With chlorotrifluoroethene, no interaction was observed: after being heated together at 220 °C in a sealed tube, unreacted (7) was recovered. However, heating (7) in a sealed tube at 100 °C for long periods, with cyclopentadiene, and with furan, afforded Diels-Alder-type adducts (11) and (12), respectively. Their analytical and mass spectroscopic data were consistent with the anticipated structures (Scheme E), as was the nmr evidence. As was expected, the latter, and glc traces also, showed that more than one isomer was present in each adduct. The major part at least of these adducts arose from isomer (7a), as was indicated by the presence in the nmr spectra of the peak due to the group $O\cdot C\mathit{F}(CF_3)\cdot Rf$. Neither of these mixtures of isomeric adducts could be separated into individual components.

OBSERVATIONS ON THE DEHYDROFLUORINATION REACTIONS

From the polyfluorodifluoromethylfurans, on dehydrofluorination by the KOH/benzene system, there were formed no compounds with an exocyclic alkene bond (loss of H from the difluoromethyl group plus the adjacent tertiary F). This is not surprising; in the polyfluorocyclohexane field, exocyclic alkene groups do not arise from analogous difluoromethyl-substituted compounds, although tertiary F substituents are fairly readily eliminated in dehydrofluorination processes [11]. The reaction of the monohydro-compound (8), with an aqueous basic system, did take place at the $-CHF_2$ group (see Scheme D), but with no certainty that the primary intermediate was an exocyclic alkene.

Again not surprisingly, no polyfluoro(methylfuran) was found among any of the products, other than possibly in very minor amounts. Drastic conditions were needed for dehydrofluorinations to give polyfluorofurans [5]. Also, polyfluorodiethyl ethers required forcing conditions for dehydrofluorination to occur [12], and the products obtained had structures typified as follows:

$$CHF_2\cdot CHF\cdot O\cdot CHF\cdot CHF_2 \longrightarrow CHF{=}CF\cdot O\cdot CHF\cdot CHF_2 \longrightarrow CHF{=}CF\cdot O\cdot CF{=}CHF$$

In all cases, H came from the α-carbon and F from the β-carbon. Thus, it appears that reactions of this type, involving loss of fluorine from positions alongside oxygen, do not proceed at all readily.

Further, $-CF_2-CHF-CHF-CF_2-$ groups, in the polyfluorocyclo-pentane [13], -hexane [3] and -heptane [14] series, preferentially lose HF from within the >CHF moieties, ie. units such as $-CF_2-CH{=}CF-CF_2-$ are formed. Hence, formation of 3,4-oxolens from precursors (IX), (X), (XII), (XIII), (IV) and (V), (H at both C-3 and C-4) accords with precedent from two different sets of results.

The mixture of substrates having a 2-trifluoromethyl group, and one H, either at position 3 or 4 (I, IIa, IIb, III) was dehydrofluorinated to give mainly oxolen (7a), again a 3,4- ene, but in admixture (9:1) with an isomer, the 2,3-oxolen (7b). Compounds (IIa) and (III) must have given (7a) exclusively, but for (I) and (IIb), loss of the tertiary F from C-2 (adjacent to oxygen) was more difficult than from the difluoromethylene group at C-4.

However, the mixed 2-difluoromethyl analogues (VIa, VIb, VII, VIII) did not behave in quite the same way, affording the corresponding 3,4- (5) and 2,3- (6) difluoromethyl-oxolens in 2:1 ratio. (VII) and (VIII) must have given only (5) , but both (5) and (6) were shown to arise from (VIa + VIb). Tertiary F in these last must be stabilized less effectively, by $-CHF_2$, than are those of I and IIb, by $-CF_3$. Thus, for (VIa + VIb), ease of HF loss from $-O-C\mathit{F}(CHF_2)-CF\mathit{H}-$ approached that from $-C\mathit{F}_2-CF\mathit{H}-$. Unfortunately, (VIa) and (VIb) could not be separated, and so it was impossible to determine whether either of them gave oxolen (5) or (6) exclusively.

The influence of stereochemical factors on the formation of 3,4-oxolens from the 3H,4H-oxolans is of interest. Of the difluoromethyl-compounds, to give oxolens (1) and (2), the 3H/4H-isomers (IX) and (X) react by syn-periplanar (or cis) elimination of HF, whilst the 3H,4H/-isomers (XII) and (XIII) react by anti-periplanar (or trans) elimination.

The following argument on the likely effects of preferred ring conformations on these eliminations is best followed with the aid of molecular models. Considering firstly the 3H,4H/-oxolans (XII) and (XIII): if trans-coplanar elimination of HF is to be achieved, then their rings have to be in C_2-like conformations, and not C_s-like (or envelope). Two such C_2 conformations are possible for (XII); in one of them the $-CHF_2$ group occupies an "axial" position, and in the other an "equatorial". The latter is obviously the more stable, and it has only the H at C-4 and the F at C-3 trans-coplanar. Elimination of these leads to the 3H-oxolen (1), which, in fact, constituted 97% of the material isolated. Likewise, (XIII) has "axial" H at C-3 and 'axial' F at C-4 in its most stable conformation, thereby leading to the 4H-oxolen (2): experimentally, 85% of (2) was found.

The 3H/4H-difluoromethyl-oxolans (IX) and (X) react by cis-eliminations and molecular models suggest that the most suitable geometries for them would involve C_s-like conformations, with the oxygen atoms out of the ring-plane. Cis-elimination should then be capable of proceeding with loss of either pair of collateral H and F substituents. Experimentally, both of the 3,4-oxolens (1) and (2), the former in slight excess, were obtained from both substrates; respectively, 58% and 42% from (IX), and 63% and 37% from (X) (Scheme A).

A competitive experiment was carried out, in which all four stereoisomers (IX, X, XII and XIII) in admixture, were treated in the standard way by KOH in suspension in benzene, and the rates of disappearance monitored by analytical glc. It seemed that all reacted at roughly similar rates, though overlapping of the glc peaks from benzene and (IX) caused difficulties with that isomer. Polyfluorocyclopentanes with 1H/2H- and with 1H,2H/- moieties differ little in their rates of loss of HF [13], and both cis- and trans-eliminations are involved. A similar situation applies to analogous polyfluorocycloheptanes also [14]. The molecular geometries of polyfluoro-oxolans are comparable to those of both of these carbocycles, as far as elimination reactions of this type are concerned.

The 3H/4H-trifluoromethyl-oxolans (IV) and (V) might have been expected to behave very similarly to compounds (IX) and (X). In fact, both afforded each of the 3,4-oxolens (3) and (4), but in significantly different proportions. The 4H/3H,2-trifluoromethyl-isomer (IV) gave 30% of (3) and 70% of (4), whilst the 3H/4H-isomer (V) gave 74% of (3) and 26% of (4) (Scheme B). For each oxolan precursor, the H on the opposite side of the ring plane to the trifluoromethyl group is the one retained in the predominant product, but it is not clear why.

A dehydrofluorination reaction was carried out on oxolan (IX) in which KOH in deuterium oxide was the basic medium. After some 50% of (IX) had reacted, it was shown by mass spectrometry that the deuterium contents of product (1) and of recovered (IX) were over 50% and ≈20% respectively. Whatever the elimination pathway involved, some carbanion formation occurs in this alkaline medium.

Long reaction times were needed for this dehydrofluorination of (IX) by KOH/D_2O, but the same products, and in similar proportions, were formed as by the system involving KOH in benzene suspension. Others of these oxolans were dehydrofluorinated using aqueous KOH, to make the oxolens for the further studies described in this paper. In all cases, the products were the same (and found in similar ratios) as those made from KOH/benzene. Hence, it seems that the results described above, using the latter reagent, can be compared directly with those from our usual aqueous KOH systems.

EXPERIMENTAL

Dehydrofluorination of Fluoro-methyloxolans by Potassium Hydroxide/Benzene

Powdered potassium hydroxide, benzene (both freshly dried) and the oxolan were stirred together at <u>ca</u> 17 °C in a flask protected by a drying tube. When glc analysis of samples indicated complete reaction (7-24 hr), the contents of the flask were vacuum-distilled to give a colourless solution. This was separated by preparative glc, using a Pye Series 104 chromatograph, having a flame-ionization detector, the tube (9.1m x 7mm i.d.; column A) being packed with Ucon L.B. 550X on Chromasorb P 30-60 (1:4). This was used also in the analytical tube (1.7m x 4mm i.d.; column B). Experiments are listed in Table 1. Glc separations were carried out with column A at a temperature of 100 °C, and nitrogen flow-rates of 3 lh^{-1}, to give pure samples of the oxolen products, with characterization data given in Tables 2-4.

TABLE 1

Details of dehydrofluorination experiments

Substrate		KOH	C_6H_6	Crude Product	Wt. used for	Sub-fractions isolated		
No.	Wt. (g)	(g)	(cm^3)	Wt. (g)	glc (g)	No.	Wt. (g)	Compound
1X	3.0	3.0	5.0	4.1	2.8	(i)	Trace	-
						(ii)	Trace	-
						(iii)	0.55	(1)
						(iv)	0.40	(2)
						(v)	1.2	benzene
X	2.1	3.0	3.0	3.7	3.7	(i)	0.75	(1)
						(ii)	0.45	(2)
						(iii)	1.55	benzene
XII	2.0	2.0	2.0	2.5	2.3	(i)	0.65	(1)
						(ii)	0.02	(2)
						(iii)	1.0	benzene
XIII	1.5	2.0	2.0	2.1	2.1	(i)	Trace	-
						(ii)	Trace	-
						(iii)	0.07	(1)
						(iv)	0.40	(2)
						(v)	0.85	benzene
IV	2.0	2.0	2.0	2.0	2.0	(i)	0.10	(3)
						(ii)	0.24	(4)
						(iii)	1.3	benzene

<u>*(continued)*</u>

TABLE 1 *(cont.)*

Substrate No.	Substrate Wt. (g)	KOH (g)	C_6H_6 (cm^3)	Crude Product Wt. (g)	Wt. used for glc (g)	Sub-fractions isolated No.	Wt. (g)	Compound
V	2.0	2.0	2.0	2.5	2.5	(i)	0.56	(3)
						(ii)	0.20	(4)
						(iii)	1.3	benzene
VIa VIb VII VIII [a]	3.0	3.0	3.0	3.7	3.7	(i)	0.82	(5)
						(ii)	0.20	(6)
						(iii)	2.0	benzene
I IIa IIb III [a]	3.0	3.0	3.0	3.7	3.7	(i)	1.0	[b](7a) + (7b)
						(ii)	2.0	benzene

[a] For these two runs, glc column (A) was run at temperatures of 70 °C.

[b] Ratio of 7a : 7b = 9 : 1 (from ^{19}F nmr).

TABLE 2

Boiling points and infrared data for compounds (1)-(8) (all are new)

Number	Name of Compound	b.p. (°C)	Infrared bands[a] C=C*H*	CF_2H	C=C
(1)	3H,2-difluoromethyltetrafluoro-3,4-oxolen	65.5	3140,	2990	1720*
(2)	4H,2-difluoromethyltetrafluoro-3,4-oxolen	75.5	3140,	2990	1715*
(3)	3H,2-trifluoromethyltetrafluoro-3,4-oxolen	47-48	3140	-	1720*
(4)	4H,2-trifluoromethyltetrafluoro-3,4-oxolen	50.5	3150	-	1720*
(5)	2-difluoromethylpentafluoro-3,4-oxolen	47-47.5	-	2990	1800′
(6)	2-difluoromethylpentafluoro-2,3-oxolen	56	-	2980	1750ˋ
(7a) +	2-trifluoromethylpentafluoro-3,4-oxolen	*ca* 27	-	-	1805′
(7b)	2-trifluoromethylpentafluoro-2,3-oxolen		-	-	1750ˋ
(8)	2-difluoromethylheptafluoro-oxolan	47	-	2990vw	-

[a] vapour spectra, measured in a cell with a path length of 10 cm.

* band due to >CH=CF< ; ′ band due to >CF=CF< ;

ˋ weak band from >CF=C(CF_3)- or from >CF=C(CHF_2)-.

TABLE 3

Analytical data for compounds (1)-(8)

Number		Formula	Required (%) C	H	F	Found (%) C	H	F
(1)	3H, 2-CHF$_2$-3, 4-ene	$C_5H_2F_6O$	31.3	1.0	59.4	31.4	1.0	59.3
(2)	4H, 2-CHF$_2$-3, 4-ene	*ditto*		*ditto*		31.3	1.15	59.5
(4)	4H, 2-CF$_3$-3, 4-ene	C_5HF_7O	28.6	0.5	63.3	28.4	0.5	63.1
(5)	2-CHF$_2$-3, 4-ene	*ditto*		*ditto*		28.2	0.5	63.0
(6)	2-CHF$_2$-2, 3-ene	*ditto*		*ditto*		28.7	0.4	63.4
(8)	2-CHF$_2$-oxolan	C_5HF_9O	24.2	0.4	-	24.4	0.45	-
			Accurate Mass Measurements Required			Found		
(3)	3H, 2-CF$_3$-3, 4-ene	C_5HF_7O	M-CF$_3$ = 140.9963			M-CF$_3$ = 140.9931		
(7a) + (7b)	2-CF$_3$-3, 4-ene 2-CF$_3$-2, 3-ene	C_5F_8O	M-CF$_3$ = 158.9869			M-CF$_3$ = 158.9864		
(8)	2-CHF$_2$-oxolan	C_5HF_9O	M-F = 228.9899			M-F = 228.9874		

TABLE 4

Major mass spectrometric peaks for compounds (1)-(8) (A. E. I. MS9 intrument)

Mass numbers for each peak are in brackets, the base peak being in italics.

Formula $C_5H_2F_6O$; Compound (1): M-F (173); ***M-CHF$_2$ (141)*** ; C_3HF_4 (113); C_3HF_2O (91); C_3HF_2 (75); CHF_2 (51); C_2HF (44).

Compound (2): M (192); ***M-F (173)*** ; M-CHF$_2$ (141); C_3HF_4 (113); $C_3H_2F_3$ (95); C_3HF_3 (94); C_3HF_2 (75); CHF_2 (51); C_2HF (44).

Formula C_5HF_7O ; Compound (3): M-F (191); ***M-CF$_3$ (141)*** ; C_3HF_4 (113); C_3HF_2O (91); C_3HF_2 (75); CF_3 (69); C_2HF (44).

Compound (4): Peaks were as for (3), except that for C_3HF_2O (91), which was missing, whilst one was present for C_3HF_3 (94).

Formula C_5HF_7O ; Compound (5): M (210); M-F (191); ***M-CHF$_2$ (159)*** ; C_4F_4O (140); C_3F_5 (131); C_3HF_4 (113); C_3F_4 (112); C_3F_3O (109); C_3F_3 (93); CF_3 (69); CHF_2 (51).

Compound (6): M (210); M-F (191); M-CHF$_2$ (159); C_4HF_5 (144); C_3F_5 (131); C_4HF_4 (125); C_3HF_4 (113); ***C_3F_3O (109)*** ; C_3HF_3 (94); C_3F_3 (93); CF_3 (69); CHF_2 (51).

(continued)

TABLE 4 (cont.)

Formula C_5F_8O ; Compound (7a + 7b): M (228); M-F (209); ***M-CF$_3$* (159)**; C_3F_5 (131); C_3F_3 (93); CF_3 (69).

Formula C_5HF_9O ; Compound (8): M-F (229); M-CHF_2 (197); ***C$_3$F$_7$* (169)** ; C_3HF_6 (151); C_3F_6 (150); C_3HF_5 (132); C_3F_5 (131); C_3HF_4 (113); C_2F_4 (100); C_2HF_3 (82); CHF_2 (51).

Other Dehydrofluorination Reactions

(i) Mixed 3H, 2- and 3H/2-difluoromethylhexafluoro-oxolans (VIa and VIb)

The inseparable mixture (VIa, 60 % + VIb, 40 % [1]) (1.3 g) was stirred with powdered KOH (1.3 g) and benzene (2.0 cm³) for 7 hours at ca 17 °C. Glc examination of the product revealed the presence of 2-difluoromethylpentafluoro-3,4- (5) and -2,3-oxolen (6), in the ratio 2:1, and also of benzene.

(ii) Compound (IX) by potassium hydroxide in deuterium oxide

4H/3H,2-Difluoromethylpentafluoro-oxolan (IX) (3.0 g) was stirred under reflux with KOH (3.0 g) in deuterium oxide (3.0 cm³) for 6 hours, with monitoring of the progress of the reaction by glc. Water (50 cm³) was added, and the lower layer washed with water , dried (phosphoric oxide), and distilled in vacuo. The distillate (1.25 g) separated by glc (as Table 1) gave: (i) two very small peaks of low retention time, not examined further; (ii) 3H,2-difluoromethyltetrafluoro-3,4-oxolen (1) (0.3 g); (iii) 4H,2-difluoromethyltetrafluoro-3,4-oxolen (2) (0.2 g); (iv) recovered 4H/3H,2-difluoromethylpentafluoro-oxolan (IX) (0.6 g); all were identified by ir spectra.

The mass spectrum of product (1) had two peaks, at 173 and 174, corresponding to $C_5H_2F_5O$ (see Table 4) and to C_5HDF_5O , respectively, in the ratio of 14:16. The base peak at 141 for C_4HF_4O was accompanied by another at 142 for C_4DF_4O, also in the ratio 14:16. The mass spectrum of the 'recovered' substrate (IX) had peaks at 193 and 194 for $C_5H_3F_6O$ and for $C_5H_2DF_6O$, respectively, and at 161 and 162 for $C_4H_2F_5O$ and for C_4HDF_5O, respectively, both pairs in the ratio 4:1 (compare Table 6, Ref. [1]).

Fluorinations of Oxolens over Cobaltic Fluoride

(i) 3H, 2-Difluoromethyltetrafluoro-3,4-oxolen (1)

This (1.4 g) was passed in a stream of nitrogen (1.0 l/hr⁻¹) through a small reactor (Reactor 2 of Ref. [15]) at 140 °C. The products (1.1 g) were swept into a cold trap by nitrogen (5 l/hr⁻¹). A part (0.6 g) was separated by glc (column A at 60 °C) to give:- (i) (0.06 g), (ii) (0.07 g), colourless liquids, not examined further; (iii) mixed 3H,2-difluoromethyl- and 3H/2-difluoromethylhexafluoro-oxolan (VIa + VIb) (0.35 g, identified by ir [1]).

(ii) 4H,3-Trifluoromethyltetrafluoro-3,4-oxolen (4)

In a reaction similar to (i), this (0.68 g) gave product (0.58 g), part (0.08 g) was separated into:- (i) a colourless liquid (0.02 g); (ii) 4H,2-trifluoromethylhexafluoro-oxolan (III) (0.03 g, identified by ir [1]).

(iii) 2-Difluoromethylpentafluoro-3,4-oxolen (5)

This (5.0 g) was fluorinated at 120 °C: the product was washed, dried and distilled in vacuo (5.7 g). Part (1.1 g) by glc (column A at 60 °C) gave 2-difluoromethylheptafluoro-oxolan (8) (0.65 g) (data in Tables 2-4).

Oxidation of 4H,2-difluoromethyltetrafluoro-3,4-oxolen (2)

(2) (0.6 g) was added to a stirred suspension of potassium permanganate (0.8 g) in dry acetone (50 cm³) and the mixture stirred for 1 hour at 17 °C and then refluxed for 2.5 hr. Isolation (Procedure A [16]) gave dianilinium (2-difluoromethyltrifluoro-3-oxaglutarate) (9a) (nc) (0.7 g); m.p. 194-196 °C; (Found: C, 48.4; H, 3.8; F, 22.3; N, 6.8. $C_{17}H_{17}F_5N_2O_5$ requires C, 48.1; H, 4.0; F, 22.4; N, 6.6%). This was converted [16] into the bis (S-benzylthiuronium) salt (9b) (89%); m.p. 187-188 °C (cited [2], 190-192 °C).

Reaction of Oxolan (8) with KOH in Water and Dimethyl Sulphoxide

2-Difluoromethylheptafluoro-oxolan (8) (2.0 g) was added to a stirred solution of KOH (2.0 g) in water (20 cm³) and dimethyl sulphoxide (100 cm³) at 80 °C, which immediately became yellow. After 4 hours, the cooled mixture was poured into water (300 cm³), acidified with dilute sulphuric acid, and extracted with ether. The extracts were dried, filtered and evaporated, and the residue of crude acid (10) was dissolved in ether and freshly-distilled aniline then added. The resultant precipitate was recrystallized from acetone/chloroform, to give dianilinium tetrafluoro-pent-2-en-1,5-dioate (10a) (nc) (0.6 g); m.p. 173-174 °C; (Found: C, 52.4; H, 4.2; F, 19.8; N, 7.1. $C_{17}H_{16}F_4N_2O_4$ requires C, 52.6; H, 4.2; F, 19.6; N, 7.2%).

A similar reaction was carried out, but for 10 minutes duration, and at 0 °C. Salt (10a) (0.5 g), identical to the above sample, was obtained.

In an earlier experiment, (8) (1.5 g) was added as above, at 80 °C, and then formalin solution (1 cm³; 40%v/v) in water (5 cm³). After 3 hours at

80 °C, and after work-up, the residual acidic liquid (10) was treated with a saturated aqueous solution of S-benzylthiuronium chloride. The precipitate was filtered off, washed and dried (1.0 g): it was the bis (S-benzylthiuronium) salt of tetrafluoropent-2-en-1,5-dioic acid (10b) (nc); m.p. 186-188 °C; (Found: C, 47.1; H, 4.2; F, 14.3; N, 10.4. $C_{21}H_{22}F_4N_4O_4S_2$ requires C, 47.2; H, 4.1; F, 14.2; N, 10.5%).

Diels-Alder Reactions of 2-Trifluoromethylpentafluoro-3,4-oxolen (7a)

(i) With cyclopentadiene

(7) (1.3 g) and cyclopentadiene (0.4 g) in a sealed Carius tube (12") were shaken and heated at 100 °C for 17 hours. The liquid product was separated from a polymeric solid, and then subjected to glc separation (column D; as column A, but packed with silicone gum (S.E. 30) on Universal B (1:40); temperature 120 °C). There were obtained: (i) and (ii) traces, two compounds of short retention time; (iii) (0.24 g); (iv) (0.10 g), dicyclopentadiene. Fraction (iii) was 2,3,5,5,6-pentafluoro-3-trifluoromethyl-4-oxatricyclo-$[5,2,1,0^{(2,6)}]$dec-8,9-ene (11) (nc); b.p. 175-176 °C; (Found: C, 40.8; H, 2.3; F, 52.0. $C_{10}H_6F_8O$ requires C, 40.8; H, 2.1; F, 51.7%); M/e, major peaks M (294), CF_3 (69), C_5H_6 (66).

(ii) With furan

(7) (2.0 g) and furan (2.0 g) were treated as above (100 °C; 40 hours). The liquid product (1.0 g) gave, by glc (column D, 130 °C): (i) (0.6 g), starting materials; (ii), 2,3,5,5,6-pentafluoro-3-trifluoromethyl-4,10-dioxatricyclo$[5,2,1,0^{(2,6)}]$dec-8,9-ene (12) (nc); b.p. 175-176 °C; (Found: C, 36.3; H, 1.4; F, 51.5. $C_9H_4F_8O_2$ requires C, 36.5; H, 1.4; F, 51.3%); M/e, major peaks M-F (277), C_5F_7O (209), C_4F_5O (159), C_3F_5(131), CF_3 (69), C_4H_4O (68). Glc of (12) showed the presence of four closely-spaced peaks.

NMR Spectroscopy

Spectra were measured on a Perkin-Elmer R10 spectrometer; ^1H shifts, at 60 MHz, are listed in p.p.m. to low field of tetramethylsilane; ^{19}F shifts, at 56.4 MHz, are to high field of trichlorofluoromethane; both references were used internally. Abbreviations for signals are:- b, broad; c, complex; d, doublet; m, multiplet; o, octet; p, pentet; q, quartet; s, singlet; sx, sextet; t, triplet. Solvents used were carbon tetrachloride for compounds (1) - (8) and dimethyl sulphoxide-d_6 for compounds (9) - (11). Results are given in Table 5.

TABLE 5

Nmr spectra of compounds (1) - (8) and (9) - (11)

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
(1)	H	5.64	1	$-CHF_2$	t; J_{HF} = 54
		5.64	1	3, =CH-	s
	F	73.6; 82.2	2	5, $>CF_2$	ABdd; J_{AB}= 152; J_d= 9; 12
		118.5	1	$>C\mathit{F}\cdot CHF_2$	o; J = 4.8
		131.7	1	4, =CF-	t; J = 13.2
		134.2	2	$-CF_2H$	d; J_{HF} = 54
(2)	H	5.87	1	$-CHF_2$	t; J_{HF} = 53
		5.87	1	4, =CH-	s
	F	61.5; 69.9	2	5, $>CF_2$	ABt; J_{AB} = 152; J_t = 10
		126.2	1	$>C\mathit{F}\cdot CHF_2$	m
		127.5	1	3, =CF-	m
		135.4	2	$-CF_2H$	d; J_{HF} = 52
(3)	H	5.8	-	3, =CH-	s
	F	73.8; 82.2	2	5, $>CF_2$	ABdd; J_{AB} = 153
		84.9	3	$-CF_3$	m
		121.0	1	$>C\mathit{F}\cdot CF_3$	o
		129.8	1	4, =CF-	tdd
(4)	H	5.9	-	4, =CH-	sx; J = 1
	F	62.2; 70.2	2	5, $>CF_2$	ABt; J_{AB} = 151; J_t = 8
		83.4	3	$-CF_3$	m
		128.3	2	$>C\mathit{F}\cdot CF_3$; 4, =CF-	m
(5)	H	5.8	-	$-CHF_2$	t; J_{HF} = 53
	F	70.5; 79.3	2	5, $>CF_2$	AB; J_{AB} = 143
		126.3	1	$>C\mathit{F}\cdot CHF_2$	m
		135.4	2	$-CF_2H$	d; J_{HF} = 52
		151.9	1	3, =CF-	m
		154.8	1	4, =CF-	q; J = 13
(6)	H	6.23	-	$-CHF_2$	tq; J_{HF} = 51
	F	92.0	2	5, $>CF_2$	d; J = 4.0
		119.8	2	4, $>CF_2$	dtd; J_d=12; 1.8; J_t=4
		127.0	2	$-CF_2H$	ddt; J_{HF}=51; J_d=11; J_t=4
		165.9	1	3, =CF-	m

(continued)

TABLE 5 (cont.)

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
(7a)	F	71.2; 79.6	2	5, $>CF_2$	AB; $J_{AB} = 141$
		83.7	3	$-CF_3$	m
		128.9	1	$>C\mathit{F}\cdot CF_3$	m
		152.1	} 1 {	3, $=CF-$	m
		153.0	} 1 {	4, $=CF-$	q; $J = 12.7$
(7b)	F	69.5	3	$-CF_3$	dt; $J_d = 14.2$; $J_t = 2.5$
		92.2	2	5, $>CF_2$	cm
		119.8	2	4, $>CF_2$	cm
		169.0	1	3, $=CF$	cm
(8)	H	6.05	-	$-CHF_2$	td; $J_{HF} = 51$; $J_d = 6.3$
	F	83.7	2	5, $>CF_2$	s
		126.9; 136.0	2	3, $>CF_2$	AB; $J_{AB} = 249$
		133.6; 138.8	2	$-CF_2H$	ABd; $J_{AB} = 310$; $J_{HF} = 51$
		129.5; 132.9	2	4, $>CF_2$	AB; $J_{AB} = 253$
		131.3	1	$>C\mathit{F}\cdot CHF_2$	m
(9a)	H	6.3	1	$-CHF_2$	td; $J_{HF} = 52$; $J_d = 8.3$
		7.0	10	arene ring	m
		8.65	6	$-\overset{+}{N}H_3$	s
	F	72.5; 79.6	2	4, $>CF_2$	ABdd; $J_{AB}= 147$; $J_d= 14.7$
		134.9	1	$>C\mathit{F}\cdot CHF_2$	m
		136.3	2	$-CF_2H$	ddd; $J_{HF} = 52$
(9b)	H	3.45	2	$=NH$	bs
		4.45	4	$>CH_2$	s
		6.1	1	$-CHF_2$	td; $J_{HF} = 54$; $J_d = 9$
		7.35	10	arene ring	c
		9.75	6	$-\overset{+}{N}H_3$	bs
	F	72.8; 77.6	2	4, $>CF_2$	ABdd; $J_{AB}= 141$; $J_d=18.5$
		136.3	3	$>C\mathit{F}\cdot C\mathit{F}_2H$	cm
(10E)	F	114.3	2	4, $>CF_2$	dd; $J_{3,4}=11.8$; $J_{2,4}=14.7$
		150.6; 155.7	2	$-CF=CF-$	ABt; $J_{AB} = 134$; $J_{4,3}= 11.7$; $J_{4,2}= 14.5$

(continued)

TABLE 5 *(cont.)*

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
/cont.					
(10Z)	F	103.6	2	4, $>CF_2$	dd; $J_{3,4}$=12.1; $J_{2,4}$= 9.6
		140.6	1	2, $=CF-$	dt; $J_{3,2}$= 6.8; $J_{4,2}$= 9.3
		148.4	1	3, $=CF-$	dt; $J_{2,3}$= 7.0; $J_{4,3}$=12.1
(10aE)	H	7.0	5	arene ring	m
		8.28	3	$-\overset{+}{N}H_3$	s
	F	107.6	2	4, $>CF_2$	dd; $J_{3,4}$= 18; $J_{2,4}$= 12
		147.3; 156.1	2	$-CF=CF$	ABt; J_{AB} = 134; $J_{4,3}$= 18; $J_{4,2}$= 12
(11)	H	1.7-2.5	1	$>CH_2$	bcm
		3.3	1	$\rightarrow CH$	bs
		6.25	1	$=CH-$	bs
		6.4		$=CH-$	bs
	F	72.9	5	$-CF_3$ $>CF_2$	
		74.8			d
		75.4			
		77.5			
		80.1			d
		82.2			d
		118.1	1	$-C\mathit{F}\cdot CF_3$	
		122.1			
		130.0			
		172.7	2	$\rightarrow CF$	
		173.9			
		175.7			
		179.5			

This material (11) also showed several other very small peaks, which have not been recorded

REFERENCES

1 Part XVIII of this Series: J. Burdon, P. L. Coe, J. A. Smith and J. C. Tatlow, J. Fluorine Chem., <u>*51*</u> (1991) 179.

2 Part IX of this Series: I. W. Parsons, P. M. Smith and J. C. Tatlow, J. Fluorine Chem., <u>*1*</u> (1971/72) 141.

3 J. A. Godsell, M. Stacey and J. C. Tatlow, Tetrahedron, 2 (1958) 193; R. Stephens, J. C. Tatlow and E. H. Wiseman, J. Chem. Soc. (1959) 148.

4 E. Nield, R. Stephens and J. C. Tatlow, J. Chem. Soc. (1959) 159.

5 J. Burdon, G. E. Chivers and J. C. Tatlow, J. Chem. Soc. (C) (1970) 2146.

6 J. Burdon, J. G. Campbell, I. W. Parsons and J. C. Tatlow, J. Chem. Soc. (C) (1971) 352.

7 J. D. Park, R. J. Seffl and J. R. Lacher, J. Am. Chem. Soc., 78 (1956) 59.

8 P. J. N. Brown, R. Stephens, J. C. Tatlow and J. R. Taylor, J. Chem. Soc. Perkin Trans. 1 (1972) 937; J. Battersby, R. Stephens, J. C. Tatlow and L. F. Thomas, J. Fluorine Chem., 15 (1980) 139.

9 E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 84 (1962) 866; 87 (1965) 1345.

10 L. A. Brooks and H. R. Snyder, Org. Syntheses Coll. Vol. III, (1955) 698.

11 J. Bailey, R. G. Plevey and J. C. Tatlow, J. Fluorine Chem., 39 (1988) 227.

12 M. Brandwood, P. L. Coe, C. S. Ely and J. C. Tatlow, J. Fluorine Chem., 5 (1975) 521.

13 R. J. Heitzman, C. R. Patrick, R. Stephens and J. C. Tatlow, J. Chem. Soc., (1963) 281: J. Burdon, T. M. Hodgins, R. Stephens and J. C. Tatlow, J. Chem. Soc. (1965) 2382.

14 J. A. Oliver, R. Stephens and J. C. Tatlow, J. Fluorine Chem., 22 (1983) 21.

15 J. Bailey, R. G. Plevey and J. C. Tatlow, J. Fluorine Chem., 37 (1987) 1.

16 J. Burdon and J. C. Tatlow, J. Applied Chem., 8 (1958) 293.