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HIGHLY FLUORINATED HETEROCYCLES—VII[1]

THE FLUORINATION OF 1,4-DIOXAN OVER COBALT TRIFLUORIDE AND POTASSIUM TETRAFLUOROCOBALTATE (III); THE FLUORINATION OF 1,4-OXATHIAN OVER POTASSIUM TETRAFLUOROCOBALTATE (III)

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Abstract—1,4-Dioxan has been fluorinated over cobalt trifluoride and potassium tetrafluorocobaltate (III). In both cases the bulk of the separated products were polyfluoro-1,4-dioxans, the degree of fluorination being greater with cobalt trifluoride. 1,4-Oxathian has been fluorinated over potassium tetrafluorocobaltate (III) to give a complex mixture of products; the major components (*ca.* 80% of the mixture) have been identified, most proved to be polyfluoro-1,4-oxathians. The mechanisms and fluorination pathways of these reactions are discussed, radical, cationic, and radical-cation type intermediates being postulated. None of the products isolated had been rearranged to the 2-methyl-1,3-dioxolan or 2-methyl-1,3-oxathiolan skeletons.

As PART of our general programme on the mechanism of fluorination with high valency transition metal fluorides (HVMFs), we have recently reported a number of fluorinations [2, 3] in which the repeated occurrence of aromatic intermediates seemed probable. In an attempt to separate the effects due to differing aromaticities from those due to differing heteroatoms, and to see if unsaturated compounds were formed, even when no aromatics could possibly be, we have fluorinated 1,4-dithian,[1] dioxan, and oxathian. Clearly, no aromatic intermediate can be formed in any of these cases. We have already reported the fluorination of 1,4-dithian;[1] rearrangement to polyfluoro-2-methyl-1,3-dithiolans predominated here and was rationalised by a carbonium ion mechanism. No unsaturated compounds were isolated, although we did postulate unsaturated intermediates.

We now report our results on the fluorination of 1,4-dioxan (dioxan) with cobalt trifluoride and with potassium tetrafluorocobaltate (III)[4] ($KCoF_4$) and the fluorination of 1,4-oxathian (oxathian) with the latter reagent; we shall concentrate on two points, the mechanism of the fluorination and the overall degree of fluorination of the products. We have used conditions similar to those previously employed for the fluorinations of tetrahydrofuran,[2, 5] thiophen[3] and dithian[1] in order to facilitate comparisons.

The structures of the products were allocated by the combination of elemental analysis, mass spectroscopy, ^1H and ^{19}F NMR spectroscopies and by chemical means. We have assigned structures to all the single products isolated, and to components of some mixtures; we are ourselves confident of their correctness but we cannot claim that they are proved beyond doubt—although certain features are certainly correct —and we have taken due account of this in the discussion sections.

DIOXAN FLUORINATIONS

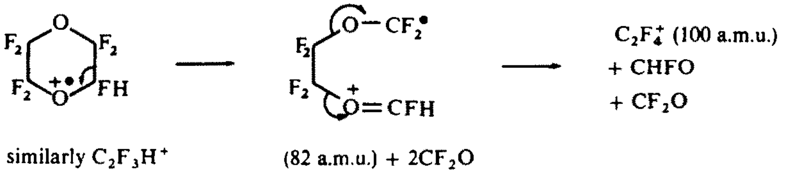
All the products isolated from both fluorinations, except two (see later), were polyfluorodioxans, and their gross structures were given by a combination of elemental analysis and ^{19}F NMR. Thus, owing to rapid conformational flipping, the tetrafluorodioxans all show a single broad doublet at ϕ 120–160 (J_{HF} ~ 45 Hz), except for the 2H/3H,5H,6H-isomer, which displays four such peaks and whose structure is thus proved. Pentafluorodioxans show three such peaks, together with an AB pattern at ϕ 70–90 (J_{AB} ~ 180 Hz), and all the hexafluorodioxans, again owing to rapid conformational equilibria, show one AB pattern and one high field doublet. The heptafluoro-compound shows a complex pattern to low field, and a single broad doublet to high field. 2,2,3-Trifluorodioxan resembles a hexafluorodioxan in its ^{19}F spectrum, but its ^{1}H spectrum shows great differences. The ^{1}H spectra are not generally very informative, being too heavily coupled for simple analysis, but they are all consistent with the assigned structures.

All the ^{19}F spectra have been analysed as simple AB patterns or on a first order basis; although this will give slightly false values of coupling constants, the values of the chemical shifts obtained should be close enough to the true values to enable them to be used with confidence in the chemical shift parameter fit.[6]

Mass spectroscopy has proved valuable: although molecular ions were weak for most compounds, all showed strong ions due to polyfluoroethylene fragments, and we suggest that a strong ion for such a fragment is good evidence for the presence of that fragment in the parent molecule.

Diagram 1 shows a likely mechanism.

DIAGRAM 1

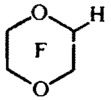
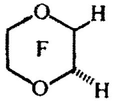
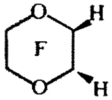
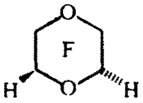
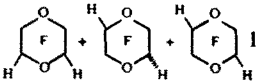
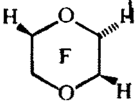
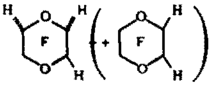
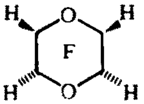
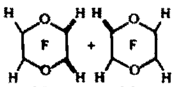
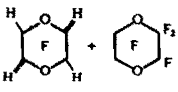


A certain amount of rearrangement clearly occurs on electron impact, since some compounds displayed peaks for $C_2F_5^+$, $C_2F_4H^+$ and $C_2F_3H_2^+$. The ethylene fragmentation route seems fairly soundly based, however, especially when extended to the oxathians, which show a similar type of behaviour (see later). By this means the monohydro-compound, the two 2H,3H-hexafluorodioxans and 2,2,3-trifluorodioxan are established. The presence of 2H,3H/-hexafluorodioxan in admixture with a pentafluorodioxan of similar retention time is also attested to. The mass spectrometric results are displayed in table 1.

We have also employed the technique of pyrolysis over AlF_3 to isomerise such compounds as we could obtain both pure and in quantity. This process *cis*/*trans* isomerises fluorines α to oxygen,[5] presumably via carbonium ions. Diagram 2 illustrates this. From previous experience, we predict that this reaction should go only with great difficulty in the direction 2H/3H- → 2H,3H/-, since the latter moiety is always relatively unstable in cyclic polyfluoro systems.

We have, in fact, carried out three such isomerisations, on the 2H/6H- and 2H/3H-hexafluorodioxans and on the 2H/3H,5H-pentafluoro-compound. The pyrolysis of

TABLE 1. SELECTED MASS-SPECTRAL DATA FOR POLYFLUORODIOXANS[a]

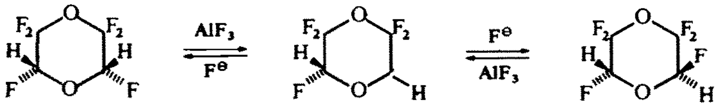
			m/e in a.m.u.					
Compound[c]	M	(M-19)	119	101	100	83	82	64
			(C_2F_5)	(C_2F_4H)	(C_2F_4)	($C_2F_3H_2$)	(C_2F_3H)	($C_2F_2H_2$)
	<1	1	10	15	100	5	46	<1
	1	2	7	8	100	17	8	42
	0·2	0·5	4	4	100	9	6	29
	0·2	0·4	<1	14	2	16	100	2
 [mixture]	1	2	<1	1	13	7	100	2
	0·5	1	1	3	14	13	100	43
	1 for each	1 for each	4	5	100	12	40	40
	4	1	<1	<1	1	10	13	100
 20% 80%	8	1	<1	<1	<1	7	3	100
 12% 88%[b]	4 (tetra F)	1						
	45 (tri F)	2	<1	<1	3	7	100	61

[a] Intensities shown are as percentages of the base peak

[b] CH_2CH_2 intensity 10

[c] 'F' inside ring denotes all unmarked bonds are to fluorine

DIAGRAM 2



the first gave a small amount of its 2H,6H/- isomer, and the (more difficult) isomerisation of the second yielded a very small amount of the 2H,3H/-compound, thus establishing the 2H,5H pair by elimination, although not showing which is the 2,6-pair and which the 2,5. The isomerisation of the third compound gave a fair yield of the 2H,5H/3H-isomer, for which the 2H,3H/-structural unit is therefore ruled out, and a very small amount of a much longer retained material, presumably the 2H,3H/5H-compound, which could not be isolated.

At this point we still need to assign which pair of hexafluorodioxans are the 2,6 and which the 2,5; and for all the polyfluorodioxans except 2,2,3-trifluorodioxan, heptafluorodioxan and 2H/3H,5H,6H-tetrafluorodioxan, stereochemistries are required (*e.g.* which of the 2H,3H pair is 2H/3H and which 2H 3H/-hexafluorodioxan). These final structural features were all assigned by a ^{19}F NMR chemical shift parameter fit, which is discussed fully in a companion paper.[6] For the remainder of this paper we will assume that these assignments are correct, although there are doubts.

The remaining two compounds from the CoF_3 fluorination present no difficulty. The ethane is known,[7] and the methyl ethyl ether shows clear ^{1}H and ^{19}F NMR spectra, besides having a correct top mass peak.

The products obtained from the two dioxan fluorinations are displayed in Tables 3 and 4, together with their percentages in the mixture.

TABLE 3. COMPOSITION OF PRODUCT MIXTURE FROM THE FLUORINATION OF 1,4-DIOXAN OVER COBALT TRIFLUORIDE

No.[a]	Compound	Percentage by weight
I	2H-Heptafluorodioxan	22·0
II	2H/3H-Hexafluorodioxan	12·0
III	2H,3H/-Hexafluorodioxan	trace
IV	2H,6H/-Hexafluorodioxan	2·2
V	2H/6H-Hexafluorodioxan	12·6
VI	2H/5H-Hexafluorodioxan	4·5
VII	2H,5H/-Hexafluorodioxan	2·2
VIII	2H/3H,5H-Pentafluorodioxan	20·4
IX	2H,5H/3H-Pentafluorodioxan	5·6
X	2H,3H/5H-Pentafluorodioxan	1·5
XII	2H,6H/3H,5H-Tetrafluorodioxan	2·6
	1,1,2-Trifluoroethane	6·5
	Difluoromethyl-1,2,2-trifluoroethyl ether	6·6
	Unknown mixtures	2·0

[a] for numbers see part VIII

TABLE 4. PERCENTAGES OF MAJOR COMPONENTS IN THE PRODUCT FROM THE FLUORINATION OF 1,4-DIOXAN OVER POTASSIUM TETRAFLUOROCOBALTATE (III)

No.[a]	Compound	Percentage by weight
XI	2H/3H,5H,6H-Tetrafluorodioxan	3·2
XII	2H,6H/3H,5H-Tetrafluorodioxan	4·8
XIII	2H,3H/5H,6H-Tetrafluorodioxan	3·3
XIV	2H,5H/3H,6H-Tetrafluorodioxan	8·9
XV	2,2,3-Trifluorodioxan	65·0

[a] Numbers in part VIII.

DISCUSSION

Two things immediately stand out from these two tables. First, that the CoF_3 products and the $KCoF_4$ products appear to be different stages on the same route, and secondly, the low degree of fluorination of the $KCoF_4$ product compared with what occurred with 1,4-dthian. In the present case the average number of fluorine atoms per product molecule is about 3·5, whereas in the dithian case this index is about 7.[1] Thus it seems well established that sulphur activates a molecule towards fluorination more than does oxygen in the equivalent situation, and we suggest that this is due to some kind of weak co-ordination between the heteroatom and the transition metal ion. Successive substitutions of fluorine α to the heteroatom will weaken this bond, and finally cause the product to be freed, at an earlier stage for oxygen than for sulphur.

It is also worthy of note that the introduction of a second heteroatom does activate the molecule further towards fluorination, as a comparison with earlier results on THF[5] clearly shows (Table 5).

TABLE 5

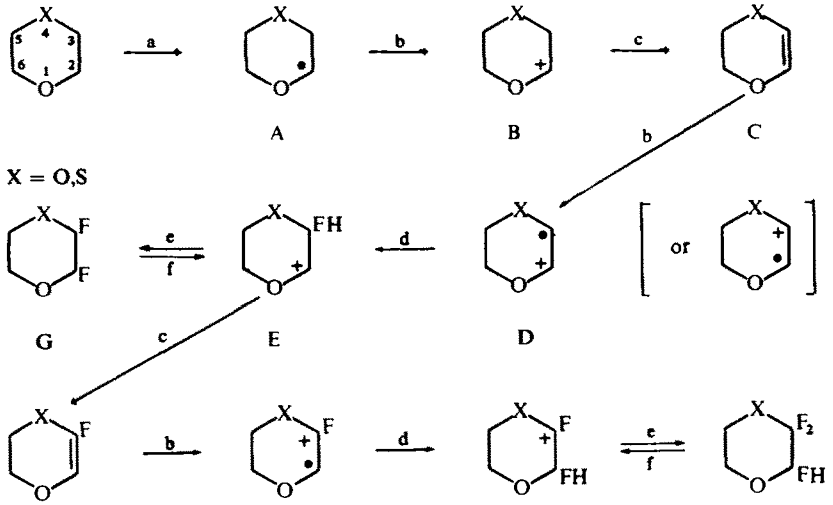
Compound type	Tetrafluoro	Pentafluoro	Hexafluoro	Heptafluoro
	% of crude fluorination mixture			
Dioxan	2·6	27·5	33·5	22·0
THF[5]	6·9	57·7	17·1	4·2

The lack of rearrangement is inconclusive, since later work on the fluorination of 2-methyl-1,3-dioxolane[8] showed that no ring-retained products were formed, the bulk of the products being polyfluoro (methyl ethyl ethers).

All the above considerations depend only on the overall degree of fluorination and gross structures of the products, and these are certainly accurate, but what follows depends to some extent on the precise structures of the compounds and is hence slightly more doubtful.

We now come to a consideration of the detailed reaction pathway. By analogy with THF,[5] we postulate initial formation of a radical, followed by that of a carbonium ion, then elimination of H^+ as HF, and rapid fluorination of the resultant double bond (diagram 3, X = O). Where a choice is possible, *e.g.* for G (diagram 3), we postulate that the ionisation route commencing with step f is favoured over a radical attack at C_6. This is justified by the result from the fluorination of THF,[5] and by the present work; most pointedly by the $KCoF_4$ results where 2,2,3 trifluorodioxan is the major product.

DIAGRAM 3. The mechanism of the fluorination of 1,4-dioxan and 1,4-oxathian by HVMF's



(Several alternatives have been omitted for clarity)

Key to reaction steps:

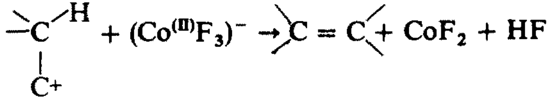
(*a*) Abstraction of H• as HF; for CoF_3

$$CoF_3 + \geqslant C{-}H \rightarrow CoF_2 + HF + \geqslant C\cdot$$

(*b*) One electron oxidation by the HVMF; *e.g.*

$$\geqslant C\cdot + Co^{(III)}F_3 \rightarrow (Co^{(III)}F_3)^- + \geqslant C^+$$

(c) Abstraction of H^+ as HF; *e.g.*



$$\geqslant C(H){-}C^+ + (Co^{(III)}F_3)^- \rightarrow\ >C=C< + CoF_2 + HF$$

(*d*) Donation of F•; *e.g.*

$$\geqslant C\cdot + CoF_3 \rightarrow \geqslant C{-}F + CoF_2$$

(*e*) Donation of F^-; *e.g.*

$$(Co^{(II)}F_3)^- + \geqslant C^+ \rightarrow CoF_2 + \geqslant C{-}F$$

(*f*) Ionisation by abstraction of fluoride; *e.g.*

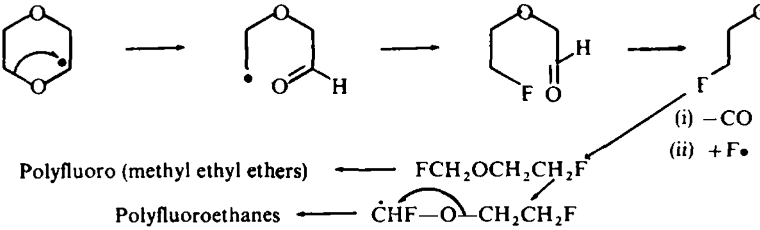
This scheme represents a slight modification of that previously presented for THF, in that no monofluorodioxan is postulated and a cation-radical species is introduced at D. We have recently come to favour such species in HVMF fluorinations for the following reasons:

(i) They provide a convincing reason for the non-isolation of unsaturated material in such fluorinations as the present one, since the ionisation potential of C (diagram 3) will be substantially less than that for a 'normal' double bond.

(ii) HVMFs are presumably good oxidants; since the related aqueous Co^{III} oxidises benzene to cation-radical species,[9] Co^{III} fluorinating agents should do the same.

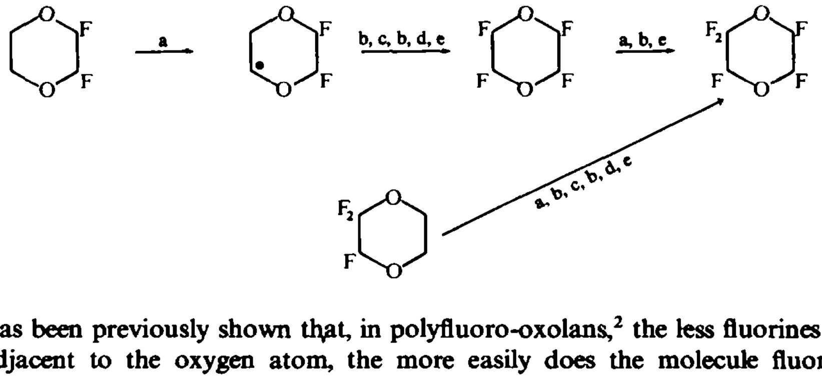
Leaving this aside, the by-products isolated may be supposed to come from A (diagram 3) as shown in diagram 4. These processes are analogous to those postulated for the cleavage of THF by CoF_3.[5]

DIAGRAM 4



Returning to the major fluorination pathway, species E may be quenched with F^- to give G, or, by a repetition of steps c, b, d and e, it may give 2,2,3-trifluorodioxan, which is the major product of the $KCoF_4$ reaction. Species G may be attacked at C_5 or C_6, thus generating the tetra- and penta-fluorodioxans. The latter are also available from the trifluorodioxan (diagram 5). It is also possible, and has been postulated before,[5] that G may revert to E by abstraction of F^-.

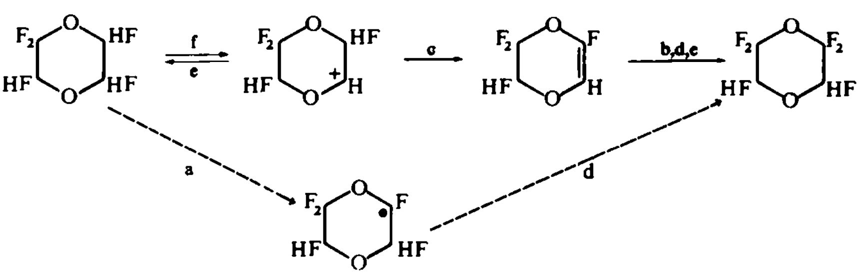
DIAGRAM 5



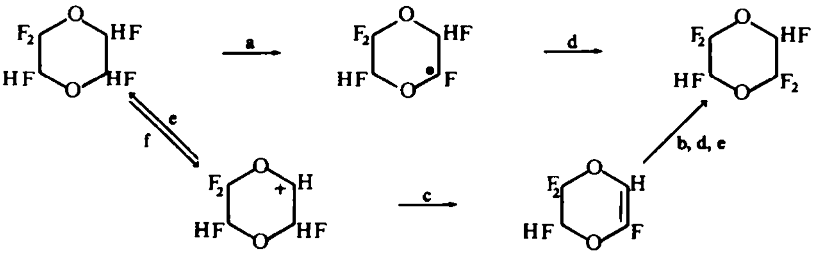
It has been previously shown that, in polyfluoro-oxolans,[2] the less fluorines there are adjacent to the oxygen atom, the more easily does the molecule fluorinate. From this it follows that further attack on the pentafluorodioxans should be predominantly at the less fluorinated end. We predict that the major hexafluoro-isomers will be the 2H,6H ones, because their formation involves reaction at the favoured end by the favoured ionization route (step f) (see diagram 6). These will fluorinate further to heptafluorodioxan faster than either the 2H,3H- or the 2H,5H-isomers.

The percentages of the isomer-pairs found for the CoF_3 reaction are as follows.

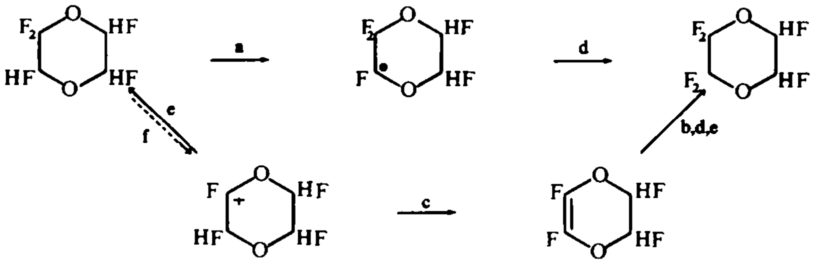
DIAGRAM 6[a]



Formation of 2H,6H-hexafluorodioxans



Formation of 2H,5H-hexafluorodioxans



Formation of 2H,3H-hexafluorodioxans.

[a] See diagram 3 for explanations of a-f: → indicates a likely route, ---→ an unlikely one.

(There is no point in distinguishing between *cis/trans* isomers here because these will be equilibrated[5] under the fluorination conditions by a mechanism akin to that described for the AlF_3 isomerisations).

2H,3H	2H,5H	2H,6H	2H
12%	6·7%	14·8%	22·0%

Thus, the 2H,6H isomers do predominate, but not, at first sight, by much. If these are indeed presumed to fluorinate faster, then the figures do support the postulated scheme.

A final point is perhaps worth making: in the CoF_3 reaction only one tetrafluorodioxan was found, but in the $KCoF_4$ mixture there were four of the possible five. Perhaps four (or five) isomers were initially formed in the CoF_3 reaction, but were isomerised to the most stable one by the ionisation reaction[5] (*c.f.* diagram 2, and diagram 3, steps e and f). We therefore propose that $KCoF_4$ is a much less active Lewis acid than is CoF_3.

OXATHIAN FLUORINATION

There are three points of major interest in this reaction: firstly, the overall degree of fluorination of the product mixture; secondly, the amount of rearrangement of the skeleton to polyfluoro-2-methyl-1,3-oxathiolans; and thirdly, the competition between the two heteroatoms for co-ordination to the HVMF surface. We have reached conclusions on the first and last points, but, for reasons to be discussed later, we are uncertain about the second. This substrate has been fluorinated only over $KCoF_4$ (III), since CoF_3 is known to remove sulphur as SF_6.

Commercial oxathian was fluorinated in the usual manner over a stirred bed of $KCoF_4$, and the products trapped at −76°. Yields were only moderate (~40%), being between those obtained for dioxan and dithian. The product was a very complex mixture, separated, with difficulty, by a combination of fractional distillation and glc.

Not all components could be obtained pure, because of their small amounts and very similar glc retention times. Those which were not isolated were mostly of short retention times, indicating they were ring-breakdown products and not germane to the main arguments of this paper.

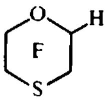
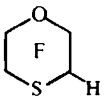
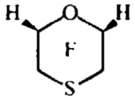
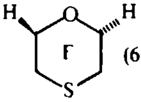
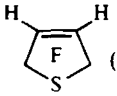
Because of the extreme difficulty of the separations, with the consequent lack of materials, and of completely pure materials in some cases, no elemental analyses have been obtained. For most of the compounds precise mass measurements have been substituted, and the elemental compositions of the products are not therefore in doubt. Similarly no bp's have been measured, but IR spectra have been obtained so that future comparisons should present no difficulty. For the same reason we have no chemical evidence (except for analogy with the dithian and dioxan reactions) for our structures, but since the spectroscopic evidence for these is very strong we feel that they are in all probability correct.

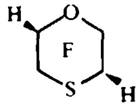
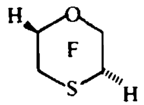
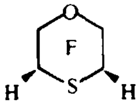
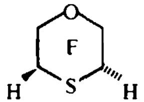
The structures of some compounds have not been established beyond showing their molecular weights by mass spectroscopy. These are polyfluorodiethyl sulphides and are of importance only in that they show either that the starting material was impure—we favour this possibility even though NMR failed to show any impurities—or that a mechanism of direct oxygen extrusion from the ring is operating. What follows refers to 1,4-oxathian structures except where otherwise stated.

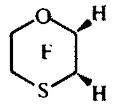
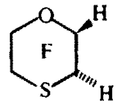
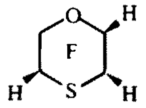
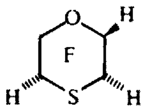
The major products by far from this reaction were polyfluoro-oxathians; their gross structures (but not the stereochemistries) were established by ^{19}F NMR and mass spectroscopy in a fairly straightforward way. Mass spectroscopy gave the molecular weight and formula, and ruled out the rearranged 2-methyl-1,3-oxathiolan structures, since these would show a very strong ion at $(M—CF_3)^+$ or $(M–CF_2H)^+$ as do the dithiolan analogues.[1]

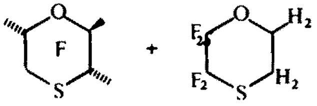
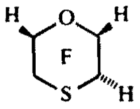
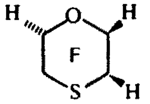
The ^{19}F spectra of several polyfluoro-oxolans,[5] -thiolans,[3] and -1,3-dithiolans[1] have been reported previously, and we report in a companion paper the spectra of some polyfluoro-1, 4-dioxans and -1,4-dithians.[6] From all this data it is possible to generalise that the CF_2 groups in such compounds show distinct differences according to whether they are α to oxygen or α to sulphur. The chemical shift ranges are heavily overlapped (*ca.* 70–95 ϕ for α oxygen,[5] and 70–105[1,3] ϕ for α to sulphur) so that this difference cannot be employed, but the geminal coupling constants are much smaller for the α-oxygen case (~140–180 Hz)[5] than for the α-sulphur (220–260 Hz).[1,3] It turns out also that there is a distinct chemical shift difference between $CH\underline{F}$

TABLE 7. SELECTED MASS SPECTRAL DATA[a] FOR THE POLYFLUORO-OXATHIANS

Structure[d]	No[b]	M^+	$(M-F)^+$	$C_2F_5^{+\cdot}$ (119)	$C_2F_4H^+$ (101)	$C_2F_4^{+\cdot}$ (100)	$C_2F_3H_2^{+\cdot c}$ (83)	$C_2F_3H^+$ (82)	$C_2F_2H_2^{+\cdot c}$ (64)	$C_2F_2H^+$ (63)	Others (intensity)
 (50%) $+CF_3$—S CFH—CF_2H (50%)	XVI	18	1	7	15	100	34	42	0	21	$CFHS^+$ (8) CF_2S^+ (21)
	XVII	25	1	5	8	34	4	100	0	9	$CFHS^+$ (28)
	XXIII	23	1	<1	21	2	10	100	0	18	$CFHS^+$ (12)
 (65%) +  (35%)	XXII	8	<1	<1	3	1	4	100	0	7	158 (16): $CFHS^+$ (5)

Structure[d]	No[b]	M^+	$(M-F)^+$	$C_2F_5^+$ (119)	$C_2F_4H^+$ (101)	$C_2F_4^+$ (100)	$C_2F_3H_2^{+\cdot c}$ (83)	$C_2F_3H^+$ (82)	$C_2F_2H_2^{+\cdot c}$ (64)	$C_2F_2H^+$ (63)	Others (intensity)
	XI	2	<1	<1	3	2	5	100	0	26	$CFHS^+$ (32)
	XX	3	<1	<1	3	<1	4	100	0	18	$CFHS^+$ (26)
	XXIV	9	<1	1	5	10	8	100	0	22	$CFHS^+$ (67)
	XXIII	11	<1	<1	4	5	5	100	0	19	$CFHS^+$ (62)

Structure[a]	No[b]	M^+	$(M-F)^+$	$C_2F_5^+$ (119)	$C_2F_4H^+$ (101)	$C_2F_4^+$ (100)	$C_2F_3H_2^{+\cdot c}$ (83)	$C_2F_3H^+$ (82)	$C_2F_2H_2^{+\cdot c}$ (64)	$C_2F_2H^+$ (63)	Others (intensity)
	XIX	16	1	3	4	94	12	0	50	37	CF_2S^+ (27) $CFHS^+$ (50)
	XVIII	14	2	3	4	70	11	10	50	37	CF_2S^+ (32) $CFHS^+$ (50)
	XXV	18	1	1	2	<1	9	92	0	16	$CHFS^+$ (100)
	XXVI	8	1	<<1	<<1	<<1	7	65	67	28	$CFHS^+$ (33)

Structure[d]	No[b]	M^+	$(M—F)^+$	$C_2F_5^+$ (119)	$C_2F_4H^+$ (101)	$C_2F_4^{+\cdot}$ (100)	$C_2F_3H_2^{+\cdot}$[c] (83)	$C_2F_3H^+$ (82)	$C_2F_2H_2^{+\cdot}$[c] (64)	$C_2F_2H^+$ (63)	Others (intensity)
 (90%) (10%)	XXVIII +XXX	5	10	<1	2	11	6	75	50	31	$CFHS^+$ (50) $(CH_2{=}CH_2)^+$ (10%)
	XXIX	4	<1	<1	2	2	6	86	67	32	$CFHS^+$ (33)
	XXVII	4	<1	<1	1	<1	6	76	50	26	$CFHS^+$ (50)

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[a] Peak intensities are quoted as % of the base peak, even where this is a composite and part of its intensity has been subtracted before its inclusion in the table.

[b] Reference numbers from Table 1

[c] These *m/e* values represent sulphur containing fragments also; they have been corrected for this where the correction was essential for the argument, *i.e.* where they are the dominant ions in the spectrum, and the S-containing fragment entered under 'others'.

[d] An 'F' inside the ring denotes all unmarked bonds to fluorine.

TABLE 8. COMPOUNDS IDENTIFIED AMONGST THE FLUORINATION PRODUCTS OF 1,4-OXATHIAN

Compound	Number[a]	%
2H-Heptafluoro-oxathian	XVI	2·2
3H-Heptafluoro-oxathian	XVII	2·0
2H/3H-Hexafluoro-oxathian	XVIII	7·8
2H,3H/-Hexafluoro-oxathian	XIX	2·1
2H/5H-Hexafluoro-oxathian	XX	6·3
2H,5H/-Hexafluoro-oxathian	XXI	2·8
2H/6H-Hexafluoro-oxathian	XXII	2·0
2H,6H/-Hexafluoro-oxathian	XXXI	1·7
3H/5H-Hexafluoro-oxathian	XXIII	7·9
3H,5H/-Hexafluoro-oxathian	XXIV	5·4
2H,3H,5H/-Pentafluoro-oxathian	XXV	1·4
2H/3H,5H-Pentafluoro-oxathian	XXVI	9·1
2H/3H,6H-Pentafluoro-oxathian	XXVIII	9·9
2H,3H/6H-Pentafluoro-oxathian	XXVII	7·0
2H,6H/3H-Pentafluoro-oxathian	XXIX	5·0
2,2,3,3-Tetrafluoro-oxathian	XXX	1·1
2,2,5,5-Tetrafluoro-3-thiolen		1·0
Trifluoromethyl 1,1,2-trifluoroethyl sulphide		2·2

[a] for numbers see part VIII

fluorines α to oxygen[5] and α to sulphur,[3] the former resonating between 130–160 φ, and the latter between 165 and 180 φ. [CHF fluorines are of course, easily distinguished from all others by a coupling of *ca.* 50 Hz to the geminal H]. The combination of these two pieces of information for the present compounds now gives the positions of the hydrogen atoms in the ring and supplies confirmation of the molecular formula.

Combination of the mass spectral and ^{19}F spectral arguments given above suffices to identify, the 2H,3H,5H- and 2H,3H,6HH-pentafluoro-oxathians, the 2H,6H- and 3H,5H-hexafluoro-oxathians and the two possible hexafluoro-oxathians, but does not distinguish between the 2H,5H- and the 2H,3H-hexafluoro-oxathians. Mass spectroscopy may be used, analogously with the dioxan case. Thus, the presence of strong ions due to, say, $C_2F_4^+$ argues for the presence of this fragment in the parent molecule; the relevant mass spectral data on the present compounds are given in Table 7. A correction has been necessary for some of the intensities, since some of the mass numbers of interest also represent sulphur-containing fragments. The intensity of a fragment ion containing ^{32}S has been calculated from that of its corresponding ^{34}S isotopic peak and this is allowed for in the table. The mass spectra are seen to fall into the expected pattern, and are entirely in accord with the ^{19}F NMR data discussed previously, except for the case of 2H,3H,5H/-pentafluoro-oxathian, which mysteriously shows no intensity for $C_2F_2H_2^+$.

The evidence for the gross structures of the polyfluoro-oxathians is thus fairly solid, and in the present paper we discuss only those features of the fluorination which depend upon the gross structures. We have, allocated precise stereochemistries to all the compounds by means of an NMR argument, but we defer a discussion of this to a companion paper.[6]

The structures of the remaining two compounds identified were assigned without any difficulty: 2,2,5,5-tetrafluoro-3-thiolen is known, and was identified *via* its molecular ion and its NMR (^{19}F and ^{1}H) spectra.[3] The structure of the hexafluoro methyl ethyl sulphide was assigned in the same way, the ^{19}F spectrum being quite characteristic (experimental).

The structures and percentages in the crude fluorination mixture of the compounds identified are shown in Table 8. These have been calculated from the peak areas of a glc trace of the crude product and are presumed to be molar. The peak area procedure is probably the best available for this complicated mixture, but we feel that the percentages of short retained materials (which includes most of the unidentified components) are probably somewhat high. Too much attention should not be paid to apparently missing oxathians (*e.g.* 2H,3H,6H/-pentafluoro-oxathian); these could well be present in the mixture but, because of their small amounts, have escaped isolation.

DISCUSSION

The overall degree of fluorination of oxathian, about 5·5 atoms of fluorine per molecule, falls evenly between those for dioxan (3·5) and dithian (7) under similar conditions, and so it seems well established that sulphur is more activating towards HVMF fluorination than oxygen, and that this activation effect is, at least qualitatively, additive. The fact that the recoveries go up with increasing substrate sulphur content also suggests that for $KCoF_4$ fluorinations, although not for CoF_3 ones, the major cause of ring breakdown involves the oxygen. We have previously discussed such a ring opening sequence (diagram 4) and the isolation of a methyl ethyl sulphide serves to substantiate this sequence in the present case.

The major products from the 1,4-dithian fluorination were mostly polyfluoro (2-methyl-1,3-dithiolans);[1] that is, rearrangement had occurred. There are at least two possible reasons for the non-appearance of rearrangement products in the oxathian and dioxan mixtures: either they are not formed, or they are destroyed by the HVMF. Our experience with the fluorination of 2-methyl-1,3-dioxolan, where no ring-retained products whatever could be isolated,[8] leads us to suppose that the latter reason may well be correct, but no definite statement is possible at this stage.

The reason for the activating effect of sulphur is not clear. The best estimate from the literature is that α-oxygen is at least 10^3 times more activating than is α-sulphur in S_N1 reactions;[10] since it is now supposed that the dominant reaction in HVMF fluorinations is a sequence involving carbonium ions and cation-radicals, such as those invoked for 1,4-dithian (we did not include radical-cations in the pathway for this compound; we would now do so) and dioxan, (diagram 3, $X = O$), it might be supposed that oxygen should be more activating than sulphur. The difference might then be ascribed to the greater β-activating ability of sulphur (a factor of 10^3–10^4 seems indicated here[11]), but it is difficult to see how this activating ability may be brought to bear without donation of lone pair electrons from the sulphur to the β-carbon atom, a process which must impose a severe strain on the ring. Also, any mechanism which involves carbonium ions would be expected, because of this much greater stabilisation of carbonium ions α to oxygen in the present system, to lead to a large bias in favour of one or the other type of product (*i.e.* most hydrogens next to oxygen or most hydrogens next to sulphur). The table shows clearly that this is not so.

Whatever is causing this equalisation of hydrogen distribution must be quite a powerful effect, since it has to overcome a factor of at least 10^3.

We suggest that the previously proposed co-ordination of the hetero-atom to the HVMF provides a simple and logical way out of this difficulty, and that, as previously discussed, sulphur co-ordinates better than oxygen, particularly towards the end of the fluorination.

In summary, these two pieces of work may be taken as supporting the previously postulated elimination/addition sequence, involving carbonium ions, for sulphur and oxygen heterocycles generally. It is also clear that sulphur does activate a molecule towards fluorination more than oxygen, but it is not as yet clear why, although we do advance a hypothesis to explain this.

EXPERIMENTAL

An entry NMR after a compound indicates that it was identified using ^{19}F NMR spectroacopy, and similarly for mass spectroscopy (MS) and infrared (IR).

Gas-liquid Chromatography Apparatus

Six preparative and semi-preparative gas-liquid chromatographic instruments were employed. A and B were Pye 104 machines, with N_2 carrier gas (20 p.s.i.); the columns were 30′ × ⅜″; A was packed with polyethyleneglycol adipate on Celite (1:6) and B with dinonyl phthalate on Celite (1:2). The remaining instruments are all of our own construction, electrically heated and employ katherometer detection systems. C, D, E, and F were 4·8 m long, Celite was the inert support and N_2 the carrier gas. Other parameters (column dia, stationary phase (ratio stationary phase/celite) N_2 flow-rate) were C (70 mm, dinonyl phthalate (1:2) 70 dm^3/hr); D (35 mm, dinonyl phthalate (1:2) 15 dm^3/hr); E (35 mm, tricresyl phosphate (1:2) 20 dm^3/hr); F (35 mm, Carbowax 35 (1:2) 15 dm^3/hr). The temp. used is given in each experiment.

Fluorination of Dioxan over CoF_3

Dioxan (250 cc) was passed into a stirred bed of CoF_3 (6 Kg; the apparatus has been described in detail before[10]) at 100° in a stream of N_2 (10 dm^3/hr). After all the dioxan had entered the reactor (3 hr) the N_2 stream was continued for a further 2 hr. The products were trapped at −78° and poured into iced water Separation gave a pale yellow liquid (90 g) which deposited crystals (1·5 g) of a tetrafluorodioxan (see later) on being stored at −60°.

The products (371 g) from four such fluorinations were washed with aq. $NaHCO_3$ and distilled from

Table 9. Distillation of CoF_3 product

Fraction No.	Wt (g)	Boiling Range
1	23·7	−10–20°
2	16·0	21–32°
3	23·1	33–39°
4	26·2	40–41°
5	17·9	42–56°
6	18·0	57–66°
7	48·1	67–70°
8	18·8	71°
9	30·2	72–75°
10	19·9	76–90°
11	32·2	91–95°
12	39·4	96–102°
13	17·7	103°

P_2O_5 up a 2′ vacuum jacketed glass column packed with Dixon gauze rings ($\frac{1}{16}$″ × $\frac{1}{16}$″). The fractions collected are shown in Table 9. A further fraction (14, 19·4 g) was distilled from the still residue at water-pump pressure.

Separation and Analysis of Fractions 1–14

Fraction 1. This was mainly (> 70% by analytical glc) 1,1,2-trifluoroethane, NMR.

Fraction 2. Separation of the whole fraction by glc (C, 60°) gave 1,1,2-trifluoroethane (1·7 g) identified by ^1H and ^{19}F NMR, and 2H-*heptafluorodioxan* (6·4 g), b.p. 39°, NMR.

Fraction 3. This was mainly (> 90% analytical glc and IR) 2H-heptafluorodioxan.

Fraction 4. A sample (5·3 g) was separated (D, 60°) into 2H-heptafluorodioxan (2·8 g) and an unidentified mixture (0·2 g).

Fraction 5. Analytical glc showed that this was 2H- heptafluorodioxan (55% by peak area), several (≥ 4) minor components (6% altogether), and difluoromethyl 1,1,2-trifluoroethyl ether (39%) (See fraction 6).

Fraction 6. Separation (C, 70°) of the whole fraction gave (i) the same minor components as in fraction 5 (2·2 g); (ii) *difluoromethyl* 1,2,2-*trifluoroethyl ether* (3·0 g) b.p. 53–54°, top mass peak 150 a.m.u. ($C_3H_3F_5O^+$); NMR. (iii) 2H/6H-*hexafluorodioxan* (5·0 g). b.p. 58° (Found: C, 24·4; H, 1·1; F, 58·6. $C_4H_2F_6O_2$ requires C, 24·5; H, 1·0; F, 58·2%), NMR. and (iv) a mixture (4·1 g) of 2H/5H-, 2H,5H/- and 2H,6H-hexafluorodioxans (in the ratios 2:1:1, according to ^{19}F NMR), b.p. 71° (Found for the mixture: C, 24·7; H, 1·0%), NMR.

Fraction 7. Analytical glc showed that this was a mixture of (ii), and (iii) and (iv) of fraction 6 in the ratios 4:12:1.

Fraction 8. This was a mixture (glc analysis) of (iii) and (iv) of fraction 6 and (iii) of fraction 9, in the ratios 1:15:20

Fraction 9. A sample (10 g) was separated (D, 60°) into (i) the mixture (iv) of fraction 6 (2·5 g) and (ii) 2H/3H-*hexafluorodioxan* (5.2 g) b.p. 72–73° (Found: C, 24·5; H, 1·1%), NMR.

Fraction 10. Separation (D, 85°) of a sample gave (i) 2H/3H-*hexafluorodioxan* (3·5 g); (ii) 2H, 5H/3H *pentafluorodioxan*, b.p. 92° (Found: C, 27·3; H, 1·5; F, 52·8. $C_4H_3F_5O_2$ requires C, 27·0; H, 1·7; F, 53·2%) NMR: and (iii) 2H/3H,5H-*pentafluorodioxan* (1·6 g) b.p. 96° (Found: C, 27·2; H, 1·9%) NMR.

Fraction 11. Analytical glc showed this to be a 1:1 mixture of 2H,5H/3H- and 2H/3H,5H-pentafluorodioxans.

Fraction 12. Separation (D, 85°) of a sample (9·9 g) gave (i) 2H/3H,5H-pentafluorodioxan, and (ii) a mixture (0·8 g) identical with (ii) of fraction 13.

Fraction 13. A sample (5·2 g) was separated (F, 115°) to give (i) 2H/3H,5H-pentafluorodioxan; and (ii) a mixture (1·2 g) which consisted (by ^{19}F NMR and analytical glc) of 2H/3H,5H-pentafluorodioxan, 2H·6H/3H,5H-tetrafluorodioxan, and two unknowns, one of which was probably 2H,3H/5H-pentafluorodioxan; and (iii) 2H,6H/3H,5H-*tetrafluorodioxan* (0·3 g) m.p. 104–107° (Found: C, 29·7; H, 2·5; F, 47·3. $C_4H_4F_4O_2$ requires C, 30·0; H, 2·5; F, 47·5) NMR; this was the same as the compound which crystallised from the crude fluorination mixture.

Fraction 14. The organic part of this (much of it was water) was very viscous and showed no peaks on analytical glc; mass spectroscopy suggested a polymeric mixture—peaks of comparable intensity for most mass numbers from 50 or so to at least 500 a.m.u.

Isomerisation of Polyfluorodioxans over AlF_3

The dioxan was passed in a stream of N_2 (1·5 dm^3/hr) through a heated (temp stated in each case) glass tube (12″ × ¾″) packed with AlF_3 powder supported on glass chips. The products were collected in a trap cooled in liquid air.

(a) 2H/6H-*Hexafluorodioxan*. 4·1 g were isomerised at 390° The product (2·3 g) was separated (E, 56°) into (i) starting material (1·2 g); and (ii) a mixture (0·7 g) of starting material (30%) and 2H,6H/-hexafluorodioxan (70%) (analysis by ^{19}F NMR).

(b) 2H/3H-*Hexafluorodioxan*. 7·4 g were isomerised at 490° (no reaction occurred at 390°). The product (5·9 g) contained very small amounts of two short retained compounds; these disappeared on standing and a white polymer was deposited. The remaining liquid product was separated (E, 85°) into (i) starting material (2·2 g): and (ii) 2H,3H/-hexafluorodioxan (0·4 g) containing some starting material (by ^{19}F NMR).

(c) 2H/3H,5H-*Pentafluorodioxan*. 4·6 g were pyrolysed at 430°. The product (2·7 g) was separated (E, 80°) into (i) an unknown compound which polymerised on standing; (ii) 2H,5H/3H-pentafluorodioxan (0·5 g); and (iii) a mixture (1·0 g) of 2H,5H/3H-pentafluorodioxan and starting material.

Fluorination of 1,4-*Dioxan over* $KCoF_4$

Dioxan (40 ml) was passed in a stream of N_2 (10 dm^3/hr) over a heated (230°) and stirred bed of $KCoF_4$ (3 kg) (the apparatus has been described before[2]). The addition took 3 hr., and the N_2 stream was continued for 2 hr. afterwards. The products were collected in a copper trap cooled to −78°; washed with water and dried to give 20·5 g of crude material.

This fluorination was very variable; sometimes the whole product polymerised with the evolution of HF and sometimes the yield was much lower than quoted.

A sample (10·5 g) of the crude product was separated (F, 100°) into (i) a mixture (0·3 g) which analytical glc suggested contained most of the products obtained from the fluorination over CoF_3; (ii) a mixture (analysis by ^{19}F NMR) (4·5 g) of $2\underline{H},5\underline{H}/3\underline{H},6\underline{H}$-tetrafluorodioxan (12%) and 2,2,3-trifluorodioxan (88%) (Found: C, 33·7; H, 3·2. Calc. for the mixture: C, 33·4; H, 3·4; Calc. for $C_4H_5F_3O_2$: C, 33·5; H, 3·5%); and (iii) a mixture, (1·3 g) which was further separated (A, 150°) into (a) $2\underline{H},6\underline{H}/3\underline{H},5\underline{H}$-tetrafluorodioxan, and (b) a mixture (4:1 by ^{19}F NMR) of $2\underline{H}/3\underline{H},5\underline{H},6\underline{H}$- and $2\underline{H},3\underline{H}/5\underline{H},6\underline{H}$-tetrafluorodioxans. (Found for the mixture: C,30·4; H, 3·5%).

The Fluorination of oxathian over $KCoF_4$

Typically, 1,4-oxathian (Koch Light) (40 ml) was fluorinated in the vapour phase at 220° over a stirred bed of $KCoF_4$ (3 kg). The apparatus[2] and technique[12] have been described before. The products were continuously eluted with N_2 (10 dm^3/hr) which was continued for 3·5 hr after the introduction of all the starting material. The products were collected in a copper vessel, cooled with solid CO_2, from which they were washed with ice water. Separation yielded a dark brown oil (28·7 g), stored at −40°. (This fluorination proved very variable.)

The bulked product (252 g) from 13 runs was washed with water before attempting distillation from P_2O_5. This distillation proved abortive, due to extensive decomposition of products, and a number of attempts were made to rectify this. Table 10 shows the weights and very approximate boiling ranges of fractions taken.

TABLE 10

Fraction No.	Wt. (g)	b.p.°	Remarks
1	1·7	5–29	2′ column;
2	1·3	30–50	Atm. press
3	24·1	50–100	No column; atm. press
4	87·7	100–125	
5[a]	23·3	20–87	6″ column; 15 mm
6	10·9	87–110	

[a] This was the residue from fraction 4, washed with water (500 cc) and extracted with ether (4 × 150 cc); the dried ($MgSO_4$) ether extracts were filtered and ether was removed by distillation through a 6″ column at atm. press.

Since the distillation proved ineffective as a separation, fraction 4 from the fractionation, which analytical glc (A, 140°) showed to contain all (*ca.* 26 components) except the very longest retained component of the crude mixture, was crudely fractionated by preparative scale glc (F, 120°) in several batches to yield cuts which were further separated. This further separation was carried out on a Pye 104 instrument, employing column A. By this means the following components of the mixture, listed in order of increasing retention time, were obtained.

(i) A mixture (1:1) of 2H-*heptafluoro-oxathian*, NMR, MS; and *trifluoromethyl*-1,2,2-*trifluoroethyl sulphide* MS ^{19}F NMR showed, for this compound, a signal at 40·3 ϕ ($CF_3 - S$), $J_D = 4$ Hz; a signal at 126·3 ϕ ($C\underline{F}_2H$—), $J_D = 54$ Hz, $J_D = 21$ Hz, $J_T = 12$ Hz; and a signal at 170·7 ϕ (S—$C\underline{F}H$—), $J_D = 49$ Hz, $J_T = 21$ Hz, $J_Q = 4$ Hz. ^1H spectroscopy showed only one signal that could be clearly assigned to this compound (owing to admixture); this was a triplet of multiplets, $J_T = 54$ Hz.

(ii) 3H-*Heptafluoro-oxathian* NMR, MS.

(iii) A mixture (2:1) of 2H/6H-*hexafluoro-oxathian* NMR; MS; and 2,2,5,5-tetrafluoro-3-thiolen NMR, MS.

(iv) 2H,6H/-*Hexafluoro-oxathian* Mass spectroscopy (Top mass peak at 212, cracking pattern in Table 2) showed this to be a hexafluoro-oxathian, and by elimination it must have the assigned structure. Insufficient material was available for NMR.

(v) An unidentified heptafluorodiethyl sulphide (Found: top mass 215·984. $C_4H_3F_7S$ requires 215·984).

(vi) An unidentified heptafluorodiethyl sulphide (Found: top mass 215·983).

(vii) 2H,5H/-*Hexafluoro-oxathian* (Found: top mass 211·975. $C_4H_2F_4OS$ requires 211·973) NMR, MS.

(viii) 2H/5H-*Hexafluoro-oxathian* (Found: top mass 211·974) NMR, MS.

(ix) 3H/5H-*Hexafluoro-oxathian* (Found: top mass 211·973) NMR, MS.

(x) 2H/3H-*Hexafluoro-oxathian* (Found: top mass 211·973) NMR, MS.

(xi) 2H,3H/-*Hexafluoro-oxathian* (Found: top mass 211·973) NMR, MS. A much weaker mass peak was evident at 193·982.

(xii) 3H/5H/-*Hexafluoro-oxathian* (Found: top mass 211·977) NMR, MS.

(xiii) A mixture (9·1) of 2H/3H,6H-*pentafluoro-oxathian* (Found: top mass 193·981. $C_4H_3F_5OS$ requires 193·982) NMR, MS, and 2,2,3,3-tetrafluoro-oxathian NMR, MS.

(xiv) 2H,6H/3H-*Pentafluoro-oxathian* (Found: top mass 193·980) NMR, MS.

(xv) 2H,3H/6H-*Pentafluoro-oxathian* (Found: top mass 193·980) NMR, MS.

(xvi) 2H3/h,5H-*Pentafluoro-oxathian* (Found: top mass 193·984) NMR, MS.

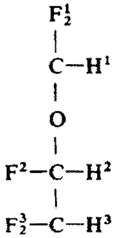
The longest retained component of the fluorination mixture was isolated from distillation fraction 6 by semi-prep. glc, as above. Fraction 6 proved to be mostly 1,4-oxathian (IR) and the long retained material proved to be

(xvii) 2H,3H,5H/-*Pentafluoro-oxathian* (Found: top mass peak 193·978) NMR, MS.

The oxathian is not included in Table 1, since it is appreciably water soluble, and its % is therefore largely meaningless.

NMR Spectroscopy. Most of the spectra are discussed in a companion paper.[6]

Difluoromethyl 1,1,2-*trifluoroethyl ether* showed, in CCl_4 soln:



$F^1_2C(H^1)\text{—}O\text{—}C(F^2)(H^2)\text{—}C(F^3_2)(H^3)$

F^1 – AB at 86·0, 86·2 ϕ, J_{AB} = 166 Hz		
F^2 at 135·5 ϕ	$J_F1_H1 = 72$;	$J_F1_{AF}2 = 7·0$;
F^3 at 146·0 ϕ	$J_F1_{BF}2 = 5·5$;	$J_F2_H2 = 57$;
H_1 at 3·60 τ	$J_F2_F3 = 7·5$;	$J_F2_H3 = 3·0$;
H_2 at 4·35 τ	$J_F3_H3 = 54$;	$J_F3_H2 = 4·5$;
H_3 at 4·35 τ	$J_H2_H3 = 4·5$ Hz	

(Couplings are not wholly reliable, owing to possible '2nd order' behaviour).

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