Highly Fluorinated Heterocycles. Part IV.[1] The Fluorination of Tetrachlorothiophen, Thiophen, and Tetrahydrothiophen over Cobaltic and Manganic Trifluorides and over Potassium Tetrafluorocobaltate(III)

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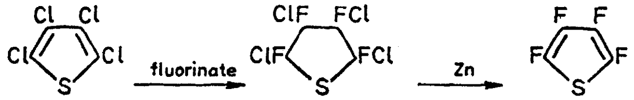
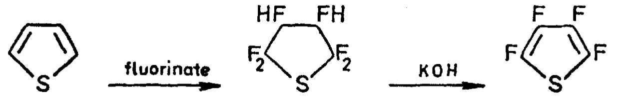
Tetrachlorothiophen reacts with cobalt trifluoride to give polychloropolyfluorobutanes and only small amounts of cyclic sulphur compounds. It reacts with potassium tetrafluorocobaltate(III) to give mainly 3,4-dichlorotetrafluoro-3-thiolen with little, if any, ring-opened products. Thiophen and tetrahydrothiophen are fluorinated by potassium tetrafluorocobaltate(III) to give product mixtures which are similar and which consist mainly of polyfluoro-thiolans and -3-thiolens. One of the major products, 3*H*/4*H*-hexafluorothiolan, can be used to prepare tetrafluorothiophen. Manganic trifluoride behaves like potassium tetrafluorocobaltate(III) with thiophen. The mechanisms of these fluorinations are discussed and it is suggested that tetrahydrothiophen is converted into thiophen before being fluorinated.

THIS paper describes our attempts to make compounds from which tetrafluorothiophen might be prepared. Initially, we had hoped to carry out the accompanying reaction sequence, which is akin to that followed by Haszeldine and his co-workers[2] in the preparation of hexafluorocyclopentadiene from hexachlorocyclopentadiene. We did not reach this objective, however, as the fluorination step did not yield any of the required tetrachlorotetrafluorothiolan. The next approach involved the fluorination of tetrahydrothiophen or thiophen, and it was successful.[3] This paper describes all these fluorinations. Three agents were employed: cobalt trifluoride, manganic trifluoride, and potassium tetrafluorocobaltate(III).



Unsuccessful reaction scheme



Successful reaction scheme

The fluorination of tetrachlorothiophen with silver difluoride has already been reported;[4] the major product was 3,4-dichlorotetrafluoro-3-thiolen (I). Silver difluoride is usually considered[5] to be a very powerful fluorinating agent, comparable with cobalt trifluoride as far as hydrocarbons are concerned, but more powerful in the replacement of chlorine by fluorine. It seemed reasonable, therefore, to expect tetrachlorothiophen to react with cobalt trifluoride or with the milder potassium tetrafluorocobaltate(III), to give less chlorine replacement than with silver difluoride and comparable, or less, ring cleavage.

It was mildly surprising, therefore (although our reaction conditions were more drastic than those employed[4] with silver difluoride), when the major products from the cobalt trifluoride–tetrachlorothiophen reaction turned out to be ring-opened compounds which had, furthermore, undergone some chlorine replacement. They were 2,2-dichloro-octafluorobutane (10%) (±)- and *meso*-2,3-dichloro-octafluorobutanes (16%), and 2,2,3-trichloroheptafluorobutane (17%); all these are known compounds[6] and they were identified by mass and ^{19}F n.m.r. spectroscopy (see Table 3 for parameters). Only

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[1] Part III, J. Burdon, G. E. Chivers, and J. C. Tatlow, *J. Chem. Soc.* (*C*), 1970, 2146.

[2] R. E. Banks, R. N. Haszeldine, and J. B. Walton, *J. Chem. Soc.*, 1963, 5581.

[3] J. Burdon, J. G. Campbell, I. W. Parsons, and J. C. Tatlow, *Chem. Comm.*, 1969, 27; *J. Chem. Soc.* (*C*), following paper.

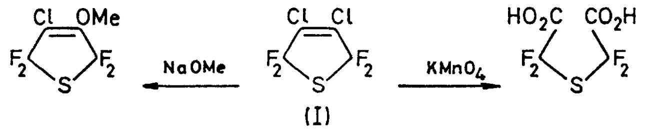
[4] H. Ulrich, E. Kober, R. Ratz, H. Schroeder, and C. Grundmann, *J. Org. Chem.*, 1962, **27**, 2593.

[5] J. C. Tatlow and M. Stacey, *Adv. Fluorine Chem.*, 1960, **1**, 166.

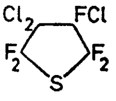
[6] A. L. Henne and T. H. Newby, *J. Amer. Chem. Soc.*, 1948, **70**, 130; U.S.P. 2,436,366 (*Chem. Abs.*, 1948, **42**, 5465g); R. N. Haszeldine, and B. R. Steele, *J. Chem. Soc.*, 1955, 3005.

a very small amount (*ca.* 1%) of one ring compound, 3,3,4-trichloropentafluorothiolan (II), was isolated from the reaction; it showed two AB patterns in its ^{19}F n.m.r. spectrum, both in positions expected[7] for $C-CF_2-S$ fluorines, and a higher field signal consistent[8] with a single C–CClF–C fluorine.

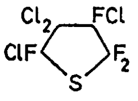
We therefore fluorinated tetrachlorothiophen with the much milder potassium tetrafluorocobaltate(III). Synthetically, the result was more useful, the major product (37%), 3,4-dichlorotetrafluoro-3-thiolen (I), being the same as the main product from silver difluoride. We identified this compound by its ^{19}F n.m.r. spectrum and further characterised it as shown. Two minor products were also isolated from our fluorination. One (2%) was 3,3,4-trichloropentafluorothiolan (II), previously obtained in the cobalt trifluoride reaction. The other (9%) also contained a CCl_2-group and was identified by ^{19}F n.m.r. spectroscopy as either the *cis*- or *trans*-isomer of either 2,3,3,4- (III) or 2,3,4,4- (IV) -tetrachlorotetrafluorothiolan; it showed one AB pattern typical[7] of a $C-CF_2-S$ group, a low-field signal consistent with one C–CFCl–S fluorine, and a higher field signal due[8] to a single C–CFCl–C fluorine.



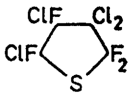
(I)



(II)



(III)



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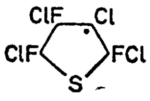
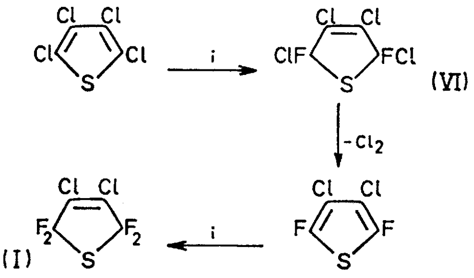


(V)

It is tempting to suppose that the major product (I) in the potassium tetrafluorocobaltate (III) and silver difluoride reactions was formed simply by a sequence (Scheme 1) of 2,5-additions of fluorine followed by 2,5-eliminations of chlorine (chlorine gas was evolved during the reaction): analogous sequences have been postulated in the fluorination of benzene[5,9] and of tetrahydrofuran.[10] It is also possible that the thiolen (VI) could be converted into the thiolen (I) by direct replacement of the allylic chlorines.

The minor potassium tetrafluorocobaltate(III) products might be formed in two ways. First, the chlorine liberated in the reaction might saturate the double bonds of the thiolens (I) or (VI); replacement of one or two chlorines by fluorine would then give the thiolans (II) and (III) [or (IV)]. Secondly, chlorine migration might occur. For example, if the thiolan (VI) were to be saturated by fluorine, the first step could be the formation of the radical (V); migration of a chlorine from the adjacent α-position would give a radical that would probably be more stable owing to the α-sulphur atom. Quenching of this new radical by fluorine would then give the thiolen (IV). The apparent specificity of the potassium tetrafluorocobaltate(III) fluorination, in that only one tetrachlorotetrafluorothiolan isomer [*cis*- or *trans*- (III) or (IV)] was isolated, is deceptive; approximately 10—15% of the reaction mixture was unidentified and might have contained other isomers with this formula.



SCHEME 1 (i) 2,5- Addition of F_2 by $KCoF_4$
X, Y = H or F

There are two extreme routes by which the polychloropolyfluorobutanes might have been formed in the cobalt trifluoride reaction. First, the fluorination could have proceeded as suggested for the potassium tetrafluorocobaltate(III) reaction as far as, say, the thiolan (II) and then the sulphur could have been extruded to give 2,2,3-trichloroheptafluorobutane; replacement of one chlorine in the latter would give the other butanes observed. Secondly, the ring might have been cleaved at the very beginning of the reaction before any fluorine had been introduced; fluorination and chlorination (or rearrangement) of the resulting n-C_4-species could then occur. We tend to favour the first alternative because the structures of the butanes resemble those of the ring compounds isolated in the potassium tetrafluorocobaltate(III) reaction, and because a reaction between tetrachlorothiophen dissolved in perfluorodecalin and cobalt trifluoride (the reaction previously described took place with tetrachlorothiophen vapour) gave a tetrachlorodifluorothiolan as the initial product. We have not investigated this liquid phase reaction thoroughly because many more products began to form as it proceeded; it was therefore valueless as a route to a tetrafluorothiophen precursor.

When thiophen was fluorinated over potassium tetrafluorocobaltate(III), a mixture of products was obtained. These were all polyfluorothiolans [(VIII), (XI), and (XIII)] or polyfluorothiolens [(VII), (IX), (X), and (XII)], except for a small amount of decafluorobutane. This contrasts with the thiophen–cobalt trifluoride trifluoride fluorination[11] where polyfluorobutanes were the major products and polyfluorothiolans the minor. The relative amounts of the products varied with temperature in the expected way; higher reaction

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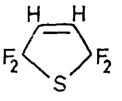
[7] (*a*) C. G. Krespan and C. M. Langkammerer, *J. Org. Chem.*, 1962, **27**, 3584; (*b*) G. V. D. Tiers, *J. Phys. Chem.*, 1962, **66**, 764.

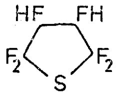
[8] T. S. Smith and E. A. Smith, *J. Phys. Chem.*, 1959, **63**, 1701.

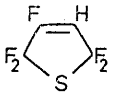
[9] P. L. Coe, R. G. Plevey, and J. C. Tatlow, *J. Chem. Soc.* (*C*), 1969, 1060.

[10] J. Burdon, G. E. Chivers, and J. C. Tatlow, *J. Chem. Soc.* (*C*), 1969, 2585.

[11] J. Burdon, J. G. Campbell, I. W. Parsons, and J. C. Tatlow, unpublished.


(VII)


(VIII)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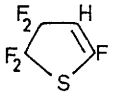
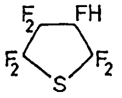
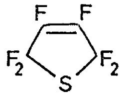
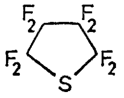

(X)


(XI)


(XII)


(XIII)

temperatutes gave higher degrees of fluorination. For example, at 120° thiophen and potassium tetrafluorocobaltate(III) gave the 3-thiolen (VII) as almost the sole product, albeit in low yield (14%), whereas at 350—370° all the compounds listed in Table 1 were present. We have concentrated on the fluorination at 350—370° because this temperature range gave the best yield of the thiolan (VIII), the tetrafluorothiophen[3] precursor. Table 1 gives a slightly false impression of the fluorination since quite a large amount of high-boiling, presumably polymeric, material was formed and this has not been taken into account in drawing up the Table. Polymer formation could account for the low yield in the 120° fluorination also, since at this temperature even low polymers would not emerge from the reactor. Further to this point, several polyfluoro-octanes were formed in the fluorination[11] of thiophen with cobalt trifluoride. Large amounts of polymeric material are not usually found[5] amongst the products of fluorination with high-valency transition-metal fluorides, although again, this could be masked by the low volatilities of such polymers. The well known acid-catalysed polymerisation of thiophen could, of course, account for the large amounts of polymer formed in the present fluorination since hydrogen fluoride is formed during the reaction.

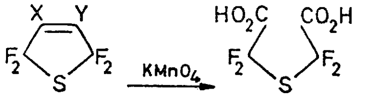
The compounds listed in Table 1 were identified in a straightforward manner. Hexafluoro-3-thiolen[12] (XII), octafluorothiolan[7a,13] (XIII), and decafluorobutane are known compounds and were identified by i.r. spectroscopy. The remaining compounds were initially identified by n.m.r. spectroscopy. This was quite simple since the CF_2–S fluorines resonated, as mentioned earlier, at lower fields than the other types (see also Table 3 for parameters). Chemical methods were also employed. Dehydrofluorination of the thiolan (VIII) with aqueous alkali gave the thiolen (IX) [molten alkali is required to convert (VIII) into tetrafluorothiophen[3]] and oxidation of this thiolen (IX) gave tetrafluoro-3-thiaglutaric acid. The thiolens (VII) and (XII) gave the same acid. It was not possible to distinguish between the *cis*-(3*H*,4*H*/-) and the *trans*-(3*H*/4*H*-) structures for (VIII) by n.m.r. spectroscopy. Comparison of boiling-points in the sequence octafluorothiolan (XIII) (b.p. 42—43°)[7a,13] 3*H*-heptafluorothiolan (XI) (b.p. 60—61°),[11] thiolan (VIII) (b.p. 74—75°) with those in the sequence octafluoro-oxolan (b.p. 1°),[14] 3*H*-heptafluoro-oxolan (b.p. 23°),[15] 3*H*/4*H*-hexafluoro-oxolan (b.p. 39°)[15] (^{19}F.n.m.r. spectroscopy[15] established the *trans*-structure quite firmly for this last compound) suggests that the thiolan (VIII) is the *trans*-(3*H*/4*H*)-isomer. Also, comparison with 1*H*-nonafluorocyclopentane, 1*H*/2*H*-, and 1*H*,2*H*/-octafluorocyclopentane[16] suggests that the *cis*-(3*H*,4*H*/-)-isomer of (VIII) would boil well above 100°.

TABLE 1

Fluorination of thiophen over $KCoF_4$ at 350—370°

Compound	Contained in fraction no.^{a}	% By wt. in fluorination mixture
3*H*,4*H*-Tetrafluoro-3-thiolen (VII)	7, 8	21
3*H*/4*H*-Hexafluorothiolan (VIII)	7, 8	25
3*H*-Pentafluoro-3-thiolen (IX)	5, 6	3
3*H*-Pentafluoro-2-thiolen (X)	5, 6	1
3*H*-Heptafluorothiolan (XI)	5, 6	11
Hexafluoro-3-thiolen (XII)	4, 5	2
Octafluorothiolan (XIII)	2, 3, 4, 5	14
Decafluoro-n-butane	1, 2	19
Thiophen	7, 8	4

^{a} See Experimental section.



Compounds (IX), (X), and (XI) could not be separated one from another and the mixture was analysed by n.m.r. spectroscopy. This was not difficult since the thiolen (IX) had been prepared in a pure state from the thiolan (VIII), and the thiolan (XI) had been isolated,[11] again in a pure state, from the fluorination of thiophen over cobalt trifluoride. Furthermore, dehydrofluorination of the mixture removed the thiolan (XI) and gave the known hexafluoro-3-thiolen[12] (XII) and hexafluoro-2-thiolen.[17] 3*H*-Pentafluoro-2-thiolen (X) is, in fact, an artifact of our isolation procedure and not a direct fluorination product, since it was not formed when the sodium fluoride scrubber (see Experimental section) was omitted from the fluorination process; it probably arises by a fluoride ion-catalysed isomerisation of the thiolen (IX). Since our main objective was to prepare the maximum amount of 3*H*/4*H*-hexafluorothiolan (VIII), we have not investigated the full consequences of omitting the sodium fluoride scrubber.

Tetrahydrothiophen gave a very similar product mixture to thiophen when fluorinated over potassium tetrafluorocobaltate(III), although higher temperatures were required to achieve comparable degrees of fluorination. Manganic trifluoride appeared to be a slightly more

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[12] (*a*) U.S.P. 2,932,651/1960 (*Chem. Abs.*, 1960, **54**, 18,549i); (*b*) U.S.P. 3,069,431/1963 (*Chem. Abs.*, 1963, **58**, 10,173h).

[13] G. V. D. Tiers, *J. Org. Chem.*, 1961, **26**, 2538.

[14] U.S.P. 2,594,272/1952 (*Chem. Abs.*, 1952, **46**, 6015a).

[15] J. Burdon, G. E. Chivers, E. F. Mooney, and J. C. Tatlow, *J. Chem. Soc.* (*C*), 1969, 1769.

[16] R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1963, 281.

[17] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, 1965, **30**, 1375.

powerful fluorinating agent than potassium tetrafluorocobaltate(III) towards thiophen since, although the same products were obtained, a comparable degree of fluorination could be achieved at a lower temperature.

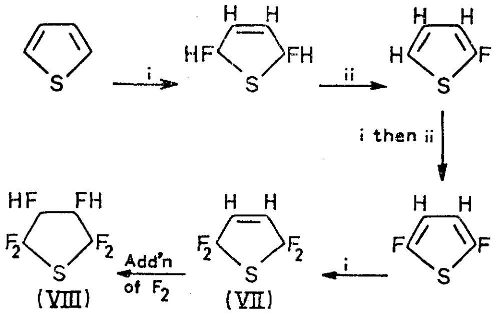
We have carried out some further experiments in an attempt to delineate the pathways taken in the thiophen and tetrahydrothiophen fluorinations. The elucidation of mechanisms by which high-valency transition-metal fluorides react is a continuing objective [5,9,10,15,16,18] in much of our present work, even when, as here, our primary purpose is the preparation of a particular polyfluorinated compound.

Since tetrahydrothiophen gave a very similar product mixture to thiophen over potassium tetrafluorocobaltate(III), it is reasonable to suppose that the former compound is converted into the latter before being fluorinated. It has previously [10] been suggested that tetrahydrofuran is converted into furan by potassium tetrafluorocobaltate(III) and that it is furan which is fluorinated and not the hydrogenated compound.

There are two obvious ways in which a saturated compound could be converted into an aromatic one; direct dehydrogenation (which might well be favoured thermodynamically at the reaction temperature) or some sequence involving potassium tetrafluorocobaltate(III) directly. Although it is known [19] that 2,5-dihydrofuran decomposes into furan and hydrogen in a noncatalytic reaction at *ca.* 400°, it does not seem that this type of direct dehydrogenation is involved in fluorination processes because passage of tetrahydrothiophen over potassium trifluorocobaltate(II) [9] at 410° gave no thiophen. However, some conversion into thiophen did occur when tetrahydrothiophen was passed over an 'exhausted'* bed of potassium tetrafluorocobaltate(III) at 350°. It seems then that potassium tetrafluorocobaltate(III) brings about the aromatization reaction by reacting with tetrahydrothiophen in some way; a number of mechanisms can be envisaged but we cannot now justify a discussion of them based on the meagre evidence at our disposal.

Thiophen itself might be fluorinated by a sequence (Scheme 2) very similar to that postulated (Scheme 1) for tetrachlorothiophen.

This leads to one of the two major products, the thiolen (VII), directly. The other, the thiolan (VIII), could be formed from it quite easily by 3,4-addition of fluorine. In accordance with Scheme 2, fluorination of the thiolen (VII) gave a product mixture which had, within experimental error, the same composition as that derived from thiophen itself. The thiolan (VIII), however, is not the sole precursor of compounds (IX)—(XIII) because fluorination of it gave a mixture which, while it contained all of (IX)—(XIII) was deficient in the thiolen (IX) as compared to the thiophen fluorination. It is possible, however, that addition of fluorine to the thiolen (VII) produces both isomers ($3H/4H$- and $3H,4H/$-) of (VIII) and that the *cis*-($3H,4H/$-) compound then reacts faster than the *trans*-($3H/4H$-), and so is not found in the fluorination mixture. Since this *cis*-isomer probably boils at over 100°, it would be difficult to separate it from the large amount of polymeric material, even if it were present. It is possible, then, that the mixed ($3H/4H$- and $3H,4H/$-) isomers of (VIII) are the precursors of (IX)—(XIII), which might arise by some or all of the following processes: (i) replacement of vinylic hydrogen by fluorine in the thiolens (VII) and (IX); (ii) dehydrofluorination of the thiolans (VIII) and (XI); (iii) replacement of hydrogen on sp^3-hybridised carbon by fluorine in the thiolans (VIII) and (XI); (iv) dehydrogenation of the thiolan (VIII); and (v) addition of fluorine to all thiolens. We feel that it is a little premature to discuss the relative merits of these reactions now.



SCHEME 2 (i), 2,5-addition of fluorine by $KCoF_4$; (ii), 2,5-elimination of hydrogen fluoride.

Decafluorobutane must arise by extrusion of sulphur in some way at some stage, but since no hydrogen-containing butanes were detected, this probably occurs when the ring is completely, or almost completely, fluorinated.

Another feature which we have not explored is the part played by the sulphur. It is possible that thiophen and the other sulphur-containing compounds could bond to the fluorinating agent by cobalt–sulphur links; this could obviously influence the position and degree of fluorination. The tetrahydrofuran fluorinations [10,15] might be similarly influenced by cobalt–oxygen co-ordination. We are currently exploring these possibilities.

EXPERIMENTAL

Fluorination of Tetrachlorothiophen over Cobalt Trifluoride.—The thiophen (10 g) was vapourised in a stream of nitrogen and passed over cobalt trifluoride (150 g) at 100° in a small, stirred reactor of the type described before.[5] The product (8·6 g) was collected in a trap cooled by liquid air (chlorine gas was allowed to escape before the product was weighed). A portion (5·1 g) was separated by g.l.c. [4·8m × 35mm tube, silicone gum on Celite (1 : 6), temp.

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* That is, one which had had a great excess of thiophen passed over it and so was probably mainly potassium trifluorocobaltate(II) containing a small amount of potassium tetrafluorocobaltate(III).

[18] A. Bergomi, J. Burdon, T. M. Hodgins, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 1966, **22**, 43.

[19] C. A. Wellington and W. D. Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 4888.

70°, N_2 flow-rate 15 dm^3/h] into (i) a mixture (3 : 2 analysed by ^{19}F n.m.r.) (1·9 g) of 2,3-dichloro-octafluorobutane [(±) and *meso*-isomers] and 2,2-dichloro-octafluorobutane, intense fragment ions at *m/e* 251 ($C_4Cl_2F_7^+$), 235 ($C_4ClF_8^+$), and 201 ($C_3Cl_2F_5^+$); (ii) 2,2,3-trichloroheptafluorobutane (1·4 g), intense fragment ions at *m/e* 267 ($C_4Cl_3F_6^+$) and 251 ($C_4Cl_2F_7^+$) [there was another, unidentified, compound present (*ca.* 10%) in (ii)]; (iii) unknown (0·1 g); (iv) unknown (0·2 g) (^{19}F n.m.r. indicated at least three compounds in each of these unknowns); and (v) 3,4,4-*trichloropentafluorothiolan* (II) (0·1 g) M^+ *m/e* 280 ($C_4Cl_3F_5S^+$).

The fluorination was also carried out by heating a stirred mixture of the thiophen (7·1 g), perfluorodecalin (100 g), and cobalt trifluoride (31·5 g) at 85—100° for 1 h. G.l.c. showed a minor product peak in addition to large peaks for solvent and starting material. Separation by g.l.c. on a 100 mm^3 scale [9 m × 9 mm tube; silicone gum on Celite (1 : 7); N_2 5 dm^3/h; temp 100°] gave (i) perfluorodecalin; (ii) a tetrachlorodifluorothiolen, intense fragment ions at *m/e* 258 ($C_4Cl_4F_2S^+$), 223 ($C_4Cl_3F_2S^+$), 204 ($C_4Cl_3FS^+$), and 188 ($C_4Cl_2F_2S^+$); and (iii) tetrachlorothiophen [(i) and (iii) were identified by i.r. spectroscopy]. When the reaction time was increased, several other products were formed.

Fluorination of Tetrachlorothiophen by Potassium Tetrafluorocobaltate(III).—The thiophen (99 g) was fluorinated over potassium tetrafluorocobaltate(III) (3 kg) at 150—170° as described before. Passage of nitrogen was continued for 2 h after all the thiophen had been added. The product (66·8 g after the chlorine had been allowed to escape) was washed with aqueous sodium bisulphite and a portion (16·1 g) of it was separated by g.l.c. [4·8 m × 75 mm column, silicone gum on Celite (1 : 6), temp. 120°, N_2 flow rate 80 dm^3/h] into (i) unknown (trace); (ii) 3,4-dichlorotetrafluoro-3-thiolen (I) (7·7 g), b.p. 122° (lit.,[4,12b] 116°) (Found: C, 20·9; F, 33·5; S, 14·2. Calc. for $C_4Cl_2F_4S$: C, 21·2; F, 33·5; S, 14·1%), M^+ *m/e* 226 ($C_4Cl_2F_4S^+$); (iii) a mixture (2·1 g, analysed by i.r. and ^{19}F n.m.r. spectroscopy) of 3,4-dichlorotetrafluoro-3-thiolen (I) (70%) and 3,3,4-trichloropentafluorothiolan (II) (30%); and (iv) 2,3,3,4- (III) [or 2,3,4,4- (IV)] tetrachlorotetrafluorothiolan (2·9 g), m.p. 122—123° (sealed tube) (Found: C, 16·2; Cl, 47·1; S, 10·8. $C_4Cl_4F_4S$ requires C, 16·1; Cl, 47·6; S, 10·8%) M^+ *m/e* 296 ($C_4Cl_4F_4S^+$). Analytical g.l.c. showed two more peaks [between (i) and (ii) and between (iii) and (iv)] but their amounts were so small that they could not be isolated.

Oxidation of 3,4-*Dichlorotetrafluoro*-3-*thiolen* (I).—The olefin (2·0 g) was oxidised with potassium permanganate in acetone.[20] The product was isolated as its anilinium salt; it was *dianilinium tetrafluoro*-3-*thiaglutarate* (0·9 g), m.p. 188—189·5° (from chloroform–acetone) (Found: C, 47·1; H, 3·9; N, 7·2. $C_{16}H_{16}F_4N_2O_4S$ requires C, 47·1; H, 3·9; N, 6·8%). This salt was converted into *bis*-S-*benzylthiuronium tetrafluoro*-3-*thiaglutarate*, m.p. 173—174° (decomp.) (from water) (Found: C, 43·2; H, 3·9; N, 10·5. $C_{20}H_{22}F_4N_4O_4S_3$ requires C, 43·3; H, 4·0; N, 10·1%).

3-*Chloro*-2,2,5,5-*tetrafluoro*-4-*methoxy*-3-*thiolen*.— 3,4-Dichlorotetrafluoro-3-thiolen (I) (3·1 g), 2·15M-sodium methoxide in methanol (7 cm^3), and methanol (20 cm^3) were kept at 15—20° for 12 h and then poured into water. The crude product (2·2 g) was isolated by ether extraction; g.l.c. showed one major (>90%) and several minor peaks. Distillation gave 3-*chloro*-2,2,5,5-*tetrafluoro*-4-*methoxy*-3-*thiolen* (1·8 g), b.p. 146—147° (Found: C, 27·2; H, 1·5. $C_5H_3ClF_4OS$ requires C, 27·0; H, 1·4%).

Fluorination of Thiophen by Potassium Tetrafluorocobaltate(III).—This was carried out at several temperatures in the range 120—450°; only two examples are described as there appeared to be a simple gradation of product compositions across the range, with most fluorine being introduced at the highest temperatures.

(a) *At* 120°. Thiophen (59 g) was passed in a stream of nitrogen (flow-rate 5 dm^3/h) during 3h through a stirred bed of potassium tetrafluorocobaltate(III) (3 kg) heated to 120°. The nitrogen stream was continued for 4 h after all the thiophen had entered the apparatus. Hydrogen fluoride was removed from the effluent by passage through a copper vessel packed with a mixture of sodium fluoride pellets and calcium oxide powder; the final product (15 g) was collected in a glass trap cooled with liquid air. G.l.c. showed three peaks, one of which comprised over 95% of the product. Purification by g.l.c. [column 4·8 m × 35 mm; silicone gum on Celite (1 : 6) temp. 80°; N_2 flow-rate 15 dm^3/h] gave 2,2,5,5-*tetrafluoro*-3-*thiolen* (VII) (7 g), b.p. 82° (Found: C, 30·0; H, 1·2. $C_4H_2F_4S$ requires C, 30·4; H, 1·3%), M^+ *m/e* 158 ($C_4H_2F_4S^+$).

This thiolen (6·0 g) and bromine (8·0 g) were irradiated in a sealed glass tube for 95 h. The reaction product was washed with aqueous sodium metabisulphite and distilled from phosphoric oxide to give 3,4-*dibromo*-2,2,5,5-*tetrafluorothiolan* (10·5 g), b.p. 158° (Found: C, 15·4; H, 0·7. $C_4H_2Br_2F_4S$ requires C, 15·1; H, 0·6%).

(b) *At* 350—370°. Thiophen (1 kg) was fluorinated in 100 g batches as in (a) but with a reactor temperature of 350—370°. The combined products (1343 g) were fractionally distilled from phosphoric oxide through a vacuum-jacketed glass column (4 ft × ½ in) packed with Dixon gauzes ($\frac{1}{16}$ in × $\frac{1}{16}$ in); the fractions taken and their weight are given in Table 2. The distillation was stopped at b.p. 77°; the residue was then a highly viscous and lachrymatory black tar which evolved hydrogen fluoride.

TABLE 2

Fraction	Wt. (g)	B.p.	Fraction	Wt. (g)	B.p.
(1)	177	0—15°	(5)	58	47—59
(2)	46	16—38	(6)	82	60—63 [a]
(3)	67	39—40	(7)	200	64—73
(4)	87	41—46	(8)	306	74—77

[a] At this point the apparatus became blocked with brown tar. This was removed by washing with acetone, and it did not subsequently re-form.

Investigation of Fractions (1)—(8).—An entry 'i.r.' indicates that the substance referred to was identified by infrared spectroscopy.

Fraction 1. This was mainly (*ca.* 90%) decafluorobutane (i.r.).

Fraction 2. This was a mixture of decafluorobutane and octafluorothiolan [7a,13] (XIII) (i.r.).

Fraction 3. This was almost (*ca.* 95%) pure octafluorothiolan [7a,13] (XIII) (i.r.).

Fraction 4. A sample (19·9 g) was separated (column 75 mm dia. × 4·8 m; dinonyl phthalate on Celite; temp. 60°; N_2 flow-rate, 40 dm^3/h) into octafluorothiolan [7a,13] (XIII) (10·0 g, i.r.), and hexafluoro-3-thiolen [12] (XII) (2·5 g, i.r.).

Fraction 5. This contained (g.l.c.) mainly the fraction (6) mixture, together with small amounts of octafluorothiolan [7a,13] (XIII) and hexafluoro-3-thiolen [12] (XII).

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[20] J. Burdon and J. C. Tatlow, *J. Appl. Chem.*, 1958, **8**, 293.

Fraction 6. ^{19}F and ^1H N.m.r. spectroscopy, i.r., and chemical evidence (see Discussion section) showed this to be a mixture of 3*H*-heptafluorothiolan (XI) (79%), 3*H*-pentafluoro-2-thiolen (X) (5%; this component was absent when the NaF/CaO trap was omitted from the fluorination apparatus), and 3*H*-pentafluoro-3-thiolen (IX) (16%); it was not resolved on g.l.c. with either dinonyl phthalate or silicone gum as stationary phases.

Fraction 7. Separation of a sample (29·6 g) (same column as in fraction (4), but at 85° and with 75 dm^3/h flow-rate) gave 3H/4H-*hexafluorothiolan* (VIII) (13·8 g), b.p. 74—75° (Found: C, 24·3; H, 1·1. $C_4H_2F_6S$ requires C, 24·5; H, 1·0%) and a mixture (9·5 g) [analysed by i.r., ^{19}F and ^1H n.m.r. spectroscopy, and g.l.c. (it separated on the analytical scale)] of 2,2,5,5-tetrafluoro-3-thiolen (VII) (60%) and thiophen (40%). The thiophen can be eliminated by carrying out the original fluorination on smaller batches.

Fraction 8. This contained (g.l.c.) 3*H*/4*H*-hexafluorothiolan (VIII) (33%), 2,2,5,5-tetrafluoro-3-thiolen (VII) (54%), and thiophen (13%).

Dehydrofluorination of 3H/4H-*Hexafluorothiolan* (VIII).—This compound (5·5 g) was heated under reflux for 5 h with 18M-potassium hydroxide (40 cm^3). G.l.c. then showed a single, product, peak. Distillation *in vacuo* from phosphoric oxide gave 3H-*pentafluoro*-3-*thiolen* (IX) (3·0 g), b.p. 60—61° [Found: C, 27·3; H, 0·6%; M^+ *m*/*e* 176 ($C_4HF_5S^+$). C_4HF_5S requires C, 27·3; H, 0·6%].

Dehydrofluorination of Fraction (6).—This fraction (21·0 g) was heated under reflux for 4·5 h with 18M-potassium hydroxide (80 cm^3). The organic layer (16·0 g) was separated by g.l.c. as before into (i) hexafluoro-3-thiolen [12] (XII) (8·2 g; i.r.), (ii) hexafluoro-2-thiolen [17] (1·1 g; i.r.), and a mixture [1·5 g; 3 : 1, analysed by ^{19}F n.m.r. spectroscopy, i.r., and by mass spectrometry (top mass peak 176—$C_4HF_5S^+$)] of 3*H*-pentafluoro-3-thiolen (IX) and 3*H*-pentafluoro-2-thiolen (X).

Oxidation of the Thiolens (VII), (IX) *and* (XII).—These thiolens were oxidised (0·5—5 g scale) with potassium permanganate in acetone as described previously.[20] The product, after conversion into its anilinium salt, in each case was dianilinium hexafluoro-3-thiaglutarate (*ca.* 60%), m.p. 187—189°, which had an i.r. spectrum identical with that of the compound prepared above.

Fluorination of 2,2,5,5-*Tetrafluoro*-3-*thiolen* (VII).—This compound (15·7 g) was fluorinated over potassium tetrafluorocobaltate(III) at 280°. The product (6·5 g) was colected in a trap cooled to −78°; no attempt was made scrub hydrogen fluoride from the effluent with NaF or CaO. A gas-liquid chromatogram of the product was very similar to that of the product from the thiophen fluorination. Separation by g.l.c. gave the same compounds (identified by i.r.) as were found in the thiophen fluorination with the exception of 3*H*-pentafluoro-2-thiolen (X). The ratio of 3*H*-heptafluorothiolan (XI) to 3-*H*-pentafluoro-3-thiolen (IX) was also very similar to that found in the thiophen fluorination [*cf.* fraction (6)].

Fluorination of 3H/4H-*Hexafluorothiolan* (VIII).—This compound (16·0 g) was fluorinated over potassium tetrafluorocobaltate at 350° [Almost no reaction occurred at at 220°] to give a mixture (10·9 g) which (g.l.c.) consisted mainly (*ca.* 60%) of the starting material. Separation of a sample by g.l.c. on a 400 mm^3 scale gave (i.r. identification) decafluorobutane, octafluorothiolan [7a,13] (XIII), hexafluoro-3-thiolen [12] (XII), 3*H*-heptafluorothiolan (XI) [containing little if any 3*H*-pentafluoro-3- and -2-thiolens (IX) and (X)], and 3*H*/4*H*-hexafluorothiolan (VIII).

Fluorination of Tetrahydrothiophen over Potassium Tetrafluorocobaltate(III).—(a) *At* 120—130°. This substrate (63 cm^3) was fluorinated as before, but at 120—130°. The

TABLE 3

^1H and ^{19}F N.m.r. spectra

	Chemical Shifts [a]	Coupling constants (Hz)
$S{\cdot}CF_2{\cdot}CCl{:}CCl{\cdot}CF_2$ 1 2 3 4 5	2-F, 76·6 [b]	
$S{\cdot}CF_2{\cdot}CCl_2{\cdot}CFCl{\cdot}CF_2$	2-F_A, 64·4; 2-F_B, 86·6; 4-F, 112·6; 5-F_A, 61·4; 5-F_B 82·6	J_{2AB}, 198; J_{5AB}, 196
$S{\cdot}CF_2{\cdot}CClF{\cdot}CCl_2{\cdot}CClF$ [c] or $S{\cdot}CF_2{\cdot}CCl_2{\cdot}CClF{\cdot}CClF$	2-F, 60·9; 3-F (or 4-F), 110·3; 5-F_A, 66·3; 5-F_B, 87·5	J_{5AB}, 196
$S{\cdot}CF_2{\cdot}CCl{:}C(OMe){\cdot}CF_2$	2-F (or 5-F), 73·5; 5-F (or 2-F) 75·3; OMe, τ 5·81	
$CF_3{\cdot}CClF{\cdot}CClF{\cdot}CF_3$	1-F, 76·2; 2-F, 130·2 [d]	
$CF_3{\cdot}CCl_2{\cdot}CClF{\cdot}CF_3$	1-F, 72·5[e]; 3-F, 120·9 [e]; 4-F, 74·5[e]	$J_{1,3}$, 5·5; $J_{1,4}$, 7·0; $J_{3,4}$, 11·0
$CF_3{\cdot}CCl_2{\cdot}CF_2{\cdot}CF_3$	1-F, 74·6; 3-F, 114·4; 4-F, 77·6	$J_{1,3}$, 11·0; $J_{1,4}$, 4·7; $J_{3,4}$, 0
$S{\cdot}CF_2{\cdot}CH{:}CH{\cdot}CF_2$	2-F, 70·1; 3-H, τ 3·74	
$S{\cdot}CF_2{\cdot}CH{:}CF{\cdot}CF_2$	2-F, 68·5; 4-F, 128·2; 5-F, 81·8; 3-H, τ 4·07	
$S{\cdot}CF{:}CH{\cdot}CF_2{\cdot}CF_2$	2-F, 106·2; 4-F, 94·6; 5-F, 92·2; 1-H, τ 4·68	
$S{\cdot}CF_2{\cdot}CF{:}CF{\cdot}CF_2$	2-F, 81·6; 3-F, 148·0	
$S{\cdot}CF{\cdot}CF{\cdot}CF_2{\cdot}CF_2$	2-F, 124·7; 3-F, 162·7; 4-F, 115·9; 5-F, 93·5	
$S{\cdot}CF_2{\cdot}CHF{\cdot}CF_2{\cdot}CF_2$ [c]	2-F_A, 2-F_B, 85·9 ; 3-F, 209·1; 4-F_A, 130·1; 4-F_B, 123·5; 5-F_A, 84·8; 5-F_B, 74·5; 3-H, τ 4·84	*J* (3-H, 3-F), 48·5; *J* (4-F_A, 4-F_B), 256; *J*(5-F_A, 5-F_B), 212
$S{\cdot}CF_2{\cdot}CHF{\cdot}CHF{\cdot}CF_2$ [c]	2-F_A, 75·5; 2-F_B, 83·2; 3-F, 204·9; 3-H, τ 4·75	*J* (2-F_A, 2-F_B) 212; *J* (3-H, 3-F), 55

[a] ^{19}F Shifts in p.p.m. upfield from internal $CFCl_3$; ^1H shifts on τ scale. [b] Cited, [4] 73·8. [c] The spectra of these compounds were only approximately AB patterns with further 1st order coupling; nevertheless we have analysed them as such. The J_{AB} might be as much as 10% in error because of this. [d] The signals were not symmetrical probably due to the presence of both [(±)-and *meso*] isomers. [e] Cited,[8] 73·3, 121·0, 75·6. [f] 2-F_A and 2-F_B have virtually identical chemical shifts.

product (21·4 g) was almost pure (*ca.* 95% by g.l.c.) 2,2,5,5-tetrafluoro-3-thiolen (VII) (i.r.).

(*b*) *At* 300°. Tetrahydrothiophen (43 cm^3) was fluorinated at 300° to give a crude product (55·7 g) which appeared (g.l.c.) to be very similar to that produced by thiophen at 220°. Separation by g.l.c. [*cf.* fraction (4), above] gave; (i) the mixture [2·8 g; i.r., *cf.* fraction (6) above] of 3*H*-heptafluorothiolan (XI), 3*H*-pentafluoro-2-thiolen (X), and 3*H*-pentafluoro-3-thiolen (IX); (ii) 3*H*/4*H*-hexafluorothiolan (VIII) (10·4 g; i.r.); and (iii) 2,2,4,4-tetrafluoro-3-thiolen (VII) (16·6 g; i.r.).

Pyrolysis of Tetrahydrothiophen over Potassium Trifluorocobaltate(II).—(*a*)Tetrahydrothiophen (20 cm^3) was passed in a stream of nitrogen over a stirred bed (the fluorination apparatus was used) of potassium trifluorocobaltate(II) [prepared by passing a large excess of thiophen over potassium tetrafluorocobaltate(III) (3 kg)] at 290°. The product (7·5 g) consisted (g.l.c.) of two components; the major one (90%) was tetrahydrothiophen and the minor (10%) thiophen.

(*b*) Tetrahydrothiophen (5 g) was passed in a stream of nitrogen over potassium trifluorocobaltate(II) (freshly prepared [9] from KF and $CoCl_2$) powder and alumina chips in a glass tube (330 mm × 15 mm) at 410°. G.l.c. showed that the product (4·3 g) contained no thiophen and was largely starting material with minor amounts of unknown decomposition products. A small amount of sulphur was deposited at the outlet of the glass tube.

Fluorination of Thiophen over Manganic Trifluoride.—Thiophen (5·4 g) was fluorinated at 300—310° in a small, stirred reactor containing manganic trifluoride (120 g). The crude product (6·8 g), whose g.l.c. was very similar to that of the fluorination product of thiophen over potassium tetrafluorocobaltate(III) at 350°, was separated to give compounds (all i.r.) (VII)—(XI) and thiophen.

N.m.r. Spectra.—These were run on a Perkin-Elmer R10 instrument at 60 MHz (^1H) and 56·4 MHz (^{19}F). Table 3 lists the parameters.

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