925. *Aromatic Polyfluoro-compounds. Part VI.** *Penta- and 2,3,5,6-Tetra-fluorothiophenol.*†

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Pentafluorothiophenol and 2,3,5,6-tetrafluorothiophenol have been prepared by reaction of sodium hydrogen sulphide in pyridine with hexa- and penta-fluorobenzene, respectively. Characterisation was effected by desulphurisation with Raney nickel. The products formed disulphides and methyl ethers. The ultraviolet and infrared absorption spectra of the compounds prepared are reported and the effects of the strongly electron-withdrawing groups briefly considered.

The susceptibility of hexa- and penta-fluorobenzene to attack by nucleophilic reagents has now been well established,[1-4] for ethers, amines, and hydrazines have been prepared. Pyridine has been used [3] as a solvent in which to prepare pentafluorophenol from hexafluorobenzene and potassium hydroxide; it had been employed earlier [5] in syntheses of derivatives such as pentachlorothiophenol from hexachlorobenzene. We now report its use in the preparation of fluorothiophenols. Both hexa- and penta-fluorobenzene reacted vigorously with sodium hydrogen sulphide in pyridine–ethylene glycol to give good yields of penta- and tetra-fluorothiophenol, respectively.

It has been suggested [5] that pyridine acts in a catalytic capacity in reactions of hexachlorobenzene with nucleophiles. A similar effect on the reaction rate was noticed with substituted pyridines such as the picolines and lutidines. A notable exception, however, was 2,6-lutidine which, although a good solvent for the system, did not effect the same increase in reaction rate; [6] this was attributed to the blocking of the hetero-nitrogen atom by the two *o*-methyl groups. Presumably the action of the pyridine is to increase the electron density around the halogen atom that is to be eliminated, and thus to assist it to escape as an ion from the aromatic nucleus.

The possibility that a penta- or tetra-fluorophenylpyridinium fluoride might be formed as an intermediate was considered. A solution of hexafluorobenzene in pyridine rapidly darkened and, after 10—15 hr. at 15°, removal of all volatile material left a dark solid which appeared from a preliminary examination to be polymeric (cf. the reaction of pyridine with octafluorocyclobutene [7]). However, under the time and temperature conditions of the reaction producing pentafluorothiophenol a good recovery of the components of the mixture (hexafluorobenzene and pyridine) was made by gas-chromatographic techniques.

Both fluoro-thiols were obtained as pungent liquids with strongly acidic properties, the potassium salts being easily recrystallised from water. It was of interest that crystalline potassium pentafluorothiophenoxide monohydrate became blue on storage; this is perhaps a consequence of the presence of thiocarbonyl groups arising from electron migrations in the crystal lattice. The absence of such a blue colour in crystals of potassium 2,3,5,6-tetrafluorothiophenoxide is significant, the necessary migrations being less easy with hydrogen in the *para*-position.

Cleavage of the carbon–sulphur linkages of each of the thiols was easily effected with Raney nickel, the corresponding fluorobenzene being produced. Thus, the product from

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* Part V, *Tetrahedron*, 1960, **9**, 240.

† The substance of this paper was reported at the International Symposium on Fluorine Chemistry, Birmingham, July, 1959.

[1] Godsell, Stacey, and Tatlow, *Nature*, 1956, **178**, 199.

[2] Forbes, Richardson, Stacey, and Tatlow, *J.*, 1959, 2019.

[3] Pummer and Wall, *Science*, 1958, **127**, 643.

[4] Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768.

[5] Rocklin, *J. Org. Chem.*, 1956, 1478.

[6] Brown and Cahn, *J. Amer. Chem. Soc.*, 1955, **77**, 1715.

[7] Pruett, Bahner, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 1638.

pentafluorobenzene gave the known 1,2,4,5-tetrafluorobenzene,[8] proving that the structure is 2,3,5,6-tetrafluorothiophenol; thus, in the reaction of pentafluorobenzene, the fluorine atom *para* to the hydrogen atom was eliminated.

In agreement with the known ease of oxidation of thiols to disulphides, the crystalline decafluorodiphenyl disulphide and octafluorodiphenyl disulphide were readily obtained from the thiophenols and one mol. of bromine in acetic acid.[9] Treatment of pentafluorothiophenol with diazomethane afforded methyl pentafluorophenyl sulphide which was oxidised by hydrogen peroxide in acetic acid to the sulphone. The analogous methyl 2,3,5,6-tetrafluorophenyl sulphide and sulphone were made similarly.

A complicating feature of the reaction of hexafluorobenzene and sodium sulphide in pyridine was the formation of an amorphous solid when the ratio of sulphide to hexafluorobenzene was less than about 1·5 : 1. A high decomposition temperature and low solubility in most solvents, coupled with an appropriate elemental analysis and consistent infrared spectrum, indicated that the solid was a perfluoropoly(phenylene sulphide). Such a polymer would arise by condensations involving the elimination of sodium fluoride. In support of this, it was found that desulphurisation with Raney nickel in butan-1-ol produced pentafluoro- and 1,2,4,5-tetrafluoro-benzene in the approximate ratio of 1 : 4, which is consistent with a *para*-linked polymer. An estimate of the molecular weight, and hence the chain length of the polymer, was impossible by normal methods owing to the very low solubility in solvents. However, if the polymer is made up exclusively of molecules of the perfluoropoly(phenylene sulphide) type (reaction iv), that is without terminal thiol groups, the ratio of pentafluoro- to tetrafluoro-benzene would indicate an average chain length of 10 units.

Pentachlorothiophenol [10] and pentafluorophenol [2] are relatively stable towards attack by nucleophiles owing to the increased electron density in the aromatic ring of the thiophenoxide and phenoxide ions. The apparent absence of a fluorobenzenedithiol from the products when hexafluorobenzene or pentafluorothiophenol was treated with sodium hydrogen sulphide in pyridine is consistent with these results. However, if pentachlorothiophenol and pentafluorophenol are etherified it has been found [10,2] that the *para*-position is rendered more susceptible to nucleophilic attack. Thus, with a deficiency of hydrogen sulphide ion in the reaction under consideration a polymer could arise by the reaction sequence depicted:

$$\mathrm{C_6F_6 + Na^+SH^- \longrightarrow C_6F_5SH + Na^+F^-} \qquad \text{(i)}$$

$$\mathrm{C_6F_5{\cdot}S^-Na^+ + C_6F_6 \longrightarrow C_6F_5{\cdot}S{\cdot}C_6F_5 + Na^+F^-} \qquad \text{(ii)}$$

$$\mathrm{C_6F_5{\cdot}S{\cdot}C_6F_5 + C_6F_5{\cdot}S^-Na^+ \longrightarrow C_6F_5{\cdot}S{\cdot}C_6F_4{\cdot}S{\cdot}C_6F_5} \qquad \text{(iii)}$$

$$\text{etc.} \longrightarrow \mathrm{C_6F_5{\cdot}[S{\cdot}C_6F_4]_{\mathit{n}}{\cdot}S{\cdot}C_6F_5} \qquad \text{(iv)}$$

The desulphurisation:

$$\mathrm{C_6F_5{\cdot}[S{\cdot}C_6F_4]_{\mathit{n}}{\cdot}S{\cdot}C_6F_5 \longrightarrow 2C_6HF_5 + \mathit{n}C_6H_2F_4} \qquad \text{(v)}$$

would be rendered unreliable in chain-length estimation to an extent depending on a reaction involving hydrogen sulphide ions, which are deficient:

$$\mathrm{C_6F_5{\cdot}S{\cdot}C_6F_5 + Na^+SH^- \longrightarrow C_6F_5{\cdot}S{\cdot}C_6F_4{\cdot}SH + Na^+F^-} \qquad \text{(vi)}$$

The possibility of nucleophilic attack on a pentafluorothiophenoxide ion appears to have been realised under drastic conditions when potassium pentafluorothiophenoxide monohydrate was heated at 250° for 5 min. The product had the same physical properties as the polymer previously described, but differences in the infrared spectra demonstrated structural differences which could arise from a change in the proportions of *ortho-*, *meta-*, and *para*-eliminations in the pyrolytic condensation. It has been found that pyrolysis of sodium pentafluorophenoxide produces some octafluorodiphenylene dioxide and a

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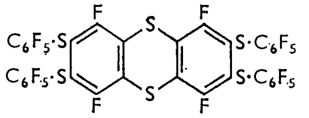
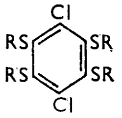
[8] Finger, Reed, Burness, Fort, and Blough, *J. Amer. Chem. Soc.*, 1951, **73**, 145.
[9] Tomiček and Valcha, *Coll. Czech. Chem. Comm.*, 1951, **16**, 113.
[10] Kulka, *J. Org. Chem.*, 1959, **24**, 235.

polymer.[11,12] Likewise, octachlorodiphenylene dioxide has been prepared by the pyrolysis of potassium pentachlorophenoxide.[13] It is possible also that further substitution of an octafluorodiphenylene disulphide, which might arise in the present work, would produce less volatile compounds of the type (I).

Such substitutions have been reported [10] to produce compounds of the type (II). Evidence that fluoride eliminations can occur in the *ortho*- and/or *meta*-positions was provided by the pyrolysis of crystalline potassium 2,3,5,6-tetrafluorothiophenoxide which gave a high-melting intractable polymer having an infrared spectrum consistent with a fluoropoly-(phenylene sulphide) but different from those of the two previously described polymers.

(I) 

 (II)

Attempts to prepare decafluorodiphenyl sulphide were unsuccessful, paralleling the observations of Pummer and Wall [11] for decafluorodiphenyl ether. Thus, the reaction of potassium pentafluorothiophenoxide with hexafluorobenzene, alone and in pyridine, gave a polymer of the perfluoropoly(phenylene sulphide) type. However, when reactants were used which prevented the building up of polymer chains, a simple sulphide was obtained; *e.g.*, potassium thiophenoxide and pentafluorobenzene gave phenyl 2,3,5,6-tetrafluorophenyl sulphide. The orientation of the latter compound was established by desulphurisation with Raney nickel to give benzene and 1,2,4,5-tetrafluorobenzene. Oxidation of this sulphide gave phenyl 2,3,5,6-tetrafluorophenyl sulphone.

A lower co-ordinating power has been reported [14] for bis(trifluoromethyl) disulphide than for dimethyl disulphide. A similar influence would be expected for the strongly electronegative fluorobenzene nuclei on the availability of the non-bonding electrons of the sulphur atom. A manifestation of this effect is believed to be the resistance to oxidation of some highly fluorinated phenyl sulphides.[15] Similar effects would be expected to be found in the ultraviolet and infrared absorption spectra. However, a direct correlation of the type observed for bis(trifluoromethyl) disulphide and trifluoromethanesulphonic acid and related compounds [14] was obscured in the present work, both in the ultraviolet and the infrared spectra, by the presence of the benzenoid nucleus.

The ultraviolet spectra of aryl sulphides and disulphides have been studied in detail,[16] and an interaction of the unbonded electrons of the sulphur atom with the electron cloud of the benzenoid nucleus reported. It would be expected, therefore, that substitution of fluorine into the benzenoid nucleus would reduce the availability of the unbonded electrons of the sulphur and result in a selective decrease in extinction coefficient. Such a decrease was observed for methyl tetra- and penta-fluorophenyl sulphide as compared with ethyl phenyl sulphide between 2500 and 2800 Å. However, this decrease is rendered less noticeable by the increase in extinction coefficient, in the range under consideration, brought about by substitution of fluorine in the benzene nucleus. This effect is clearly shown by the sulphone series: methyl tetrafluorophenyl sulphone, methyl pentafluorophenyl sulphone, methyl phenyl sulphone. In this series the removal of the sulphur lone pair destroys the previously described interaction, but the absorption maxima of the fluorinated compounds are at slightly higher wavelengths and display larger extinction coefficients than those of the unfluorinated analogue. It was also of interest to find the benzenoid fine structure present in the methyl phenyl sulphone but not in the fluoro-analogues.

[11] Pummer and Wall, unpublished results.
[12] Burdon, Richardson, and Tatlow, unpublished results.
[13] Merz and Weith, *Ber.*, 1872, **5**, 458; Sanderman, Stockmann, and Casten, *Chem. Ber.*, 1957, **90**, 690.
[14] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2549.
[15] Robson, Smith, Stephens, and Tatlow, unpublished work.
[16] Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84, 231.

Decreases in extinction coefficient were also found for the penta- and tetra-fluorothiophenols and the derived disulphides, as compared with the unfluorinated analogues, between 2300 and 2400 Å (see Table 1). Likewise, diphenyl sulphide displayed a larger extinction coefficient than phenyl 2,3,5,6-tetrafluorophenyl sulphide around 2500 Å. However, for reasons unknown, within the groups of fluorinated systems considered the extinction coefficients of the pentafluoro-type compounds are not always smaller than those of the tetrafluoro-analogues.

TABLE 1. *Ultraviolet light absorptions* (*in ethanol except as otherwise indicated*).

$\lambda_{\text{min.}}$ (Å)	$10^{-3}\varepsilon$	$\lambda_{\text{max.}}$ (Å)	$10^{-3}\varepsilon$
Pentafluorothiophenol			
2170	5·32	2300	5·91
2420	4·33	2570	5·92
Hydrated potassium pentafluorothiophenoxide in water			
		2520	14·2
Decafluorodiphenyl disulphide			
2250	10·8	2300	11·7
		2480(i)	10·3
2650	5·47	2670	5·55
Methyl pentafluorophenyl sulphide			
2350	1·80	2625	3·97
Methyl pentafluorophenyl sulphone			
2420	0·199	2720	1·65
Phenyl 2,3,5,6-tetrafluorophenyl sulphide			
		2450	6·78
2620	4·28	2740	4·87
Phenyl 2,3,5,6-tetrafluorophenyl sulphone			
2590	1·71	2700	2·46
2720	2·36	2770	2·73
		2900(i)	1·84
2,3,5,6-Tetrafluorothiophenol			
2150	6·25	2170	6·68
2200	6·27	2250	6·38
2270	6·04	2320	6·35
2350	6·25	2370	6·38
2400	6·23	2420	6·64
2720	2·58	2860	2·84
Hydrated potassium 2,3,5,6-tetrafluorothiophenoxide in water			
2300	3·64	2610	12·7
Methyl 2,3,5,6-tetrafluorophenyl sulphide			
2400	1·29	2660	5·55
Methyl 2,3,5,6-tetrafluorophenyl sulphone			
2400	0·067	2805	2·47
Bis-(2,3,5,6-tetrafluorophenyl) disulphide			
		2200	7·79
2300	6·92	2420	9·38
2600	3·33	2750	4·18
		2850(i)	3·22

= inflexion.

TABLE 2. *Infrared absorption peaks ascribed to* C–S *stretching vibration mode.*

	Peak (cm.$^{-1}$)
Pentafluorothiophenol	716
Decafluorodiphenyl disulphide	731
Methyl pentafluorophenyl sulphide	713
Methyl pentafluorophenyl sulphone	725
2,3,5,6-Tetrafluorothiophenol	711
Bis-(2,3,5,6-tetrafluorophenyl) disulphide	717
Methyl 2,3,5,6-tetrafluorophenyl sulphide	714
Methyl 2,3,5,6-tetrafluorophenyl sulphone	715
Phenyl 2,3,5,6-tetrafluorophenyl sulphide	712
Phenyl 2,3,5,6-tetrafluorophenyl sulphone	713

A markedly higher carbon–sulphur stretching frequency has been observed for bis(trifluoromethyl) disulphide (759 cm.$^{-1}$) than for dimethyl disulphide (690 cm.$^{-1}$) and this was attributed to an increase in force constant for this vibrational mode. The assignment of characteristic vibration frequencies to the carbon–sulphur bonds in molecules as complex as those described here is less certain since a large number of substituted benzene derivatives possess a band near 700 cm.$^{-1}$. Nevertheless, an absorption peak attributable to the C–S stretching vibration was observed at 717 ± 6 cm.$^{-1}$ (see Table 2). The frequency for unfluorinated aromatic systems of this type is between 600 and 700 cm.$^{-1}$.[17] The increased frequency would arise in the same way as for the aliphatic analogues.

[17] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1959, p. 353.

EXPERIMENTAL

Techniques.—Gas chromatography and infrared measurements were carried out as before,[18] unless otherwise stated.

Pentafluorothiophenol.—Hydrogen sulphide was bubbled through a solution of sodium hydroxide (12·2 g.) in ethylene glycol (20 c.c.) for 3 hr. and the resulting viscous liquid was quickly added dropwise to a boiling solution of hexafluorobenzene (10·0 g.) in pyridine (75 c.c.), with intermittent shaking. When the vigorous reaction had subsided, the mixture was refluxed for 5 min., cooled, and poured on crushed ice. The solution obtained was acidified with 16N-hydrochloric acid and extracted with ether (3 × 250 c.c.), and the combined extracts were dried ($MgSO_4$), filtered, and evaporated to a dark liquid which distilled at atmospheric pressure to give the colourless, pungent *pentafluorothiophenol* (7·1 g.), b. p. 143°, n_D^{22} 1·4622 (Found: C, 36·1; H, 0·5; S, 16·8. C_6HF_5S requires C, 36·0; H, 0·5; S, 16·0%). An infrared absorption peak at 2620 cm.$^{-1}$ indicated the presence of an S–H link and strong absorptions in the region 1500—1530 cm.$^{-1}$ are associated with the fluorinated benzene ring.

An aqueous solution of potassium hydroxide and pentafluorothiophenol gave hydrated *potassium pentafluorothiophenoxide* as colourless needles, m. p. >300°, which developed a blue colour within a few days (Found: C, 27·4; H, 0·7. $C_6F_5KS,1\frac{1}{2}H_2O$ requires C, 27·2; H, 1·1%). The S–H stretching frequency region was transparent in the infrared spectrum, but absorption peaks at 1634 and 1515 cm.$^{-1}$ were consistent with the presence of " bound " water [19] and a fluorinated benzene ring, respectively.

When pentafluorothiophenol (10·0 g.) was treated with sodium hydrogen sulphide prepared from sodium hydroxide (12·2 g.) in pyridine (80 c.c.)–ethylene glycol (20 c.c.), as described in the above preparation, the thiophenol (7·3 g.), b. p. 140—141°, was recovered.

Hexafluorobenzene (5·8 g.) and pyridine (50 c.c.) were refluxed together for 5 min. and half of the solution (25 c.c.) was then separated by gas chromatography [column B silicone gum 301 (1 pt.)–kieselguhr (4 pts.), temp. 110°, N_2 flow-rate 56 l./hr.] into hexafluorobenzene (2·4 g.) and pyridine (24 c.c.).

Desulphurisation of Pentafluorothiophenol.—Pentafluorothiophenol (5·6 g.) was added to a suspension of Raney nickel (Grade W4; 30·0 g.) in butan-1-ol (50 c.c.). When the initial vigorous reaction had subsided the mixture was refluxed for 6 hr. and then distilled through a 2′ vacuum-jacketed column packed with 1/16″ × 1/16″ Dixon gauze rings. The fraction boiling at 67—104° (4·4 g.) was separated by gas chromatography (column A, temp. 100°, N_2 flow-rate 10 l./hr.) to give, as the main fraction, pentafluorobenzene (2·8 g.) which had the correct infrared spectrum.

Decafluorodiphenyl Disulphide.—Bromine (1·0 g.) was added dropwise to a stirred solution of pentafluorothiophenol (1·6 g.) in acetic acid (10 c.c.). The acetic acid was removed by distillation *in vacuo* and the involatile brown gum, crystallised by trituration with aqueous ethanol, gave colourless needles of *decafluorodiphenyl disulphide* (0·85 g.), m. p. 50—51° (Found: C, 36·3; F, 47·7; S, 16·0. $C_{12}F_{10}S_2$ requires C, 36·2; F, 47·7; S, 16·1%). The infrared spectrum displayed strong absorption at 1515 cm.$^{-1}$ and no $\geqslant$C–H or S–H stretching frequencies.

Methyl Pentafluorophenyl Sulphide.—Methylnitrosourea (10·0 g.) was slowly added to 40% w/v aqueous potassium hydroxide (25 c.c.) and ether (40 c.c.) kept at 0°. The ether layer was then separated and to it was slowly added a solution of pentafluorothiophenol (6·0 g.) in ether (10 c.c.). After 1 hr. at room temperature the mixture was dried ($MgSO_4$), filtered, and evaporated. Distillation of the residual liquid gave *methyl pentafluorophenyl sulphide* (5·6 g.), b. p. 171—173° (Found: C, 39·6; H, 1·5; F, 43·9. $C_7H_3F_5S$ requires C, 39·3; H, 1·4; F, 44·4%). The presence of a weak band at 2960 cm.$^{-1}$ is ascribed to $\geqslant$C–H stretching vibrations; the fluorinated benzene ring vibration was displayed at 1496 cm.$^{-1}$.

Methyl Pentafluorophenyl Sulphone.—Methyl pentafluorophenyl sulphide (2·45 g.), 30% w/w hydrogen peroxide (15 c.c.), and acetic acid (10 c.c.) were kept at 100° for 2 hr. The mixture was then poured into water and the precipitate (2·3 g.) recrystallised from aqueous alcohol to give the *sulphone* (2·0 g.), m. p. 85—86° (Found: C, 33·9; H, 1·2; F, 38·7. $C_7H_3F_5O_2S$ requires C, 34·15; H, 1·2; F, 38·6%). Infrared absorption peaks at 1165 and 1347 cm.$^{-1}$ were ascribed to the $>SO_2$ group, and at 2945 and 1500 cm.$^{-1}$ to the $\geqslant$C–H and fluorinated benzene ring vibrations, respectively.

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[18] Stephens, Tatlow, and Wiseman, *J.*, 1959, 148.

[19] Levine, Stevenson, and Kabler, *Arch. Biochem. Biophys.*, 1953, **45**, 65; Forziati and Rowen, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 38.

A Perfluoropoly(phenylene Sulphide).—Hydrogen sulphide was bubbled through a solution of sodium hydroxide (4·2 g.) in ethylene glycol (18 c.c.) for 2 hr. and the resulting solution quickly added to a boiling solution of hexafluorobenzene (10·3 g.) in pyridine (75 c.c.). When the vigorous reaction had subsided the mixture was refluxed for 5 min., cooled, poured on crushed ice, and acidified with 16N-hydrochloric acid. The precipitate was washed with water and dried, to give a pale yellow amorphous material (10·7 g.), m. p. >300° (decomp.), which could not be sublimed and was soluble only in pyridine [Found: C, 38·8; H, 1·7; F, 40·6. After several hours *in vacuo* at 140° over P_2O_5: C, 40·2; H, 0. $(C_6F_4S)_n$ requires C, 40·0; H, 0; F, 42·2%]. Fusion of the *polymer* with sodium revealed the presence of fluorine and sulphur and the absence of nitrogen. The infrared spectrum of the dried solid dispersed in Nujol revealed very strong absorption peaks ascribable to fluorinated aromatic ring vibrations at 1490—1500 cm.$^{-1}$.

A suspension of the solid (9·0 g.) in butan-1-ol (140 c.c.) was refluxed with Raney nickel (Grade W4, 75 g.) for 4¾ hr. The mixture was distilled as in the previous desulphurisation. The fraction (3·5 g.), b. p. 67—94°, was shown by gas chromatography to contain six components and these were separated by preparative-scale gas chromatography into fractions with retention times identical with those of ethanol, butyraldehyde, butan-1-ol, and a mixture (0·7 g.) of 1,2,4,5-tetrafluorobenzene and pentafluorobenzene; the identities were confirmed by comparison of the infrared spectra with those of authentic specimens. The infrared spectrum of the mixture indicated an approximate ratio of tetrafluoro- to pentafluoro-benzene of 4 : 1.

A Second Perfluoropoly(phenylene Sulphide).—Potassium pentafluorothiophenoxide hydrate (1·0 g.) was heated in a hard-glass test-tube to a final temperature of about 300°. The residue was washed with water and dried to give a *polymer* (0·7 g.), m. p. >300° (Found: C, 37·6; H, 0·5; F, 39·7; S, 18·4%). The washings gave a strong cerous nitrate test for fluoride ion. Fusion of the polymer with sodium produced sodium fluoride and sodium sulphide.

Attempted Preparation of Bis(pentafluorophenyl) Sulphide.—(i) Potassium pentafluorothiophenoxide (1·0 g.) and hexafluorobenzene (0·75 g.) were kept at 160° in a sealed tube for 19 hr., then added to water. The insoluble solid (0·35 g.), m. p. >300°, was shown by infrared spectrometry to be almost identical with the polymer prepared from hexafluorobenzene and a and a deficiency of sulphide. (ii) When potassium pentafluorothiophenoxide (3·0 g.) was slowly added to hexafluorobenzene (2·7 g.) in pyridine (25 c.c.) and the mixture was refluxed for 5 min. and then poured on ice and acidified, the usual polymer (2·0 g.), m. p. >300°, was obtained. (iii) When hexafluorobenzene (5·4 g.) in pyridine (10 c.c.) was added to a warm solution of the potassium pentafluorothiophenoxide (6·0 g.) in pyridine (50 c.c.) a precipitate of potassium fluoride was produced. The mixture was then added to ice and acidified. The solid product (4·0 g.), m. p. >300°, displayed similar infrared spectrum to that of the polymer described above in (i). No sublimation was found to occur even after many hours at 200°/0·05 mm.

Phenyl 2,3,5,6-*Tetrafluorophenyl Sulphide.*—Pentafluorobenzene (3·4 g.) in pyridine (10 c.c.) was added to a solution of potassium thiophenoxide (2·3 g.) in pyridine (10 c.c.), and the mixture was refluxed for 10 min., poured into water (100 c.c.), acidified with 8N-hydrochloric acid, and extracted with ether (3 × 100 c.c.). The combined extracts were dried ($MgSO_4$), filtered, and evaporated, and the residue was distilled to give *phenyl* 2,3,5,6-*tetrafluorophenyl sulphide* (2·3 g.), b. p. 265°/760 mm., 117°/1·5 mm. (Found: C, 55·6; H, 2·3; F, 29·0. $C_{12}H_6F_4S$ requires C, 55·8; H, 2·3; F, 29·4%). Infrared absorption peaks at 2980, 1485, and 712 cm.$^{-1}$ were ascribed to vibrational modes of C–H, fluorinated benzene ring, and C–S, respectively. The sulphide (1·1 g.) with 30% w/v hydrogen peroxide (1 c.c.) in acetic acid (10 c.c.) gave a crystalline *sulphone* (1·15 g.), which, recrystallised from ethanol, had m. p. 164° (Found: C, 49·6; H, 2·2. $C_{12}H_6F_4O_2S$ requires C, 49·6; H, 2·1%).

Desulphurisation of Phenyl 2,3,5,6-*Tetrafluorophenyl Sulphide.*—The sulphide (2·0 g.) was added quickly to a suspension of Raney nickel (Grade W4; 25 g.) in butan-1-ol (200 c.c.). When the reaction had subsided, the mixture was refluxed for 5 hr. and distilled as before. A fraction (4·7 g.) of b. p. 69—104° was shown by analytical gas chromatography to contain five components which were separated by preparative-scale gas chromatography (column A, temp. 102°, N_2 flow-rate 9·3 l./hr.) into four fractions; one (0·35 g.) of these was shown by infrared spectroscopy to be a mixture of 1,2,4,5-tetrafluorobenzene and benzene. The other three fractions had gas-chromatographic retention times identical with those of ethanol, butyraldehyde, and butan-1-ol.

2,3,5,6-*Tetrafluorothiophenol.*—A solution of sodium hydrogen sulphide in ethylene glycol, prepared from sodium hydroxide (12·2 g.) as previously described, was added dropwise to a boiling solution of pentafluorobenzene (10·0 g.) in pyridine (75 c.c.), with occasional agitation. The mixture was then refluxed for 5 min., cooled, poured on crushed ice, acidified with 16N-hydrochloric acid, and extracted with ether (3 × 250 c.c.). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to leave a dark liquid which on distillation gave the pungent 2,3,5,6-*tetrafluorothiophenol* (8·7 g.), b. p. 147°, n_D^{22} 1·4827 (Found: C, 39·6; H, 1·1; F, 41·4. $C_6H_2F_4S$ requires C, 39·6; H, 1·1; F, 41·7%), $\nu_{max.}$ 3100 ($\geqslant$C–H), 2595 (S–H), and 1507 cm.$^{-1}$ (fluorinated benzene ring).

An aqueous solution of potassium hydroxide and the tetrafluorothiophenol gave hydrated *potassium tetrafluorothiophenoxide* as colourless needles, m. p. >300° (Found: C, 30·3; H, 1·4; F, 31·9. C_6HF_4KS,H_2O requires C, 30·3; H, 1·3; F, 31·9%); this compound remained colourless on storage. The infrared spectrum of the solid in Nujol contained no absorption in the S–H stretching region; absorption peaks at 1630 and 1495 cm.$^{-1}$ were ascribed to "bound" water [19] and to the fluorinated benzene ring, respectively.

Desulphurisation. The tetrafluorothiophenol (7·1 g.) was added to a suspension of Raney nickel (Grade W4; 75 g.) in butanol (75 c.c.). After being refluxed for 4 hr. the mixture was distilled as before. All the material (8·1 g.) boiling up to 98° was collected. Analytical gas chromatography revealed four main peaks which were separated by preparative-scale chromatography (temp. 100°, N_2 flow-rate 58·0 l./hr.) to give: (*a*) mixed solvents, mainly ethanol (0·5 g.); (*b*) butyraldehyde (1·85 g.); (*c*) 1,2,4,5-tetrafluorobenzene [8] (3·9 g.); (*d*) butan-1-ol (0·4 g.); components (*b*), (*c*), and (*d*) were identified by comparison of their infrared spectra with those of authentic specimens.

Methyl 2,3,5,6-*Tetrafluorophenyl Sulphide.*—A solution of 2,3,5,6-tetrafluorothiophenol (4·9 g.) in ether was slowly added to diazomethane in ether (80 c.c.), prepared from methylnitrosourea (20 g.) and 40% aqueous potassium hydroxide (50 c.c.) as previously described. The mixture was kept at 15° for 1 hr. before being dried ($MgSO_4$), filtered, and evaporated to a liquid which was distilled, giving *methyl* 2,3,5,6-*tetrafluorophenyl sulphide* (3·6 g.), b. p. 169—174°; this fraction gave only one peak in analytical gas chromatography (Found: C, 43·1; H, 2·3; F, 39·1. $C_7H_4F_4S$ requires C, 42·9; H, 2·1; F, 38·7%). $\nu_{max.}$ were at 2960 ($\geqslant$C–H) and 1500 cm.$^{-1}$ (fluorinated benzene ring).

Methyl 2,3,5,6-*Tetrafluorophenyl Sulphone.*—The 2,3,5,6-tetrafluorophenyl sulphide (1·1 g.), 30% w/w aqueous hydrogen peroxide (5 c.c.), and acetic acid (10 c.c.) at 100° for 1½ hr. gave the *sulphone* (0·2 g. from aqueous ethanol), m. p. 92—93° (Found: C, 36·6; H, 1·7; F, 33·4. $C_7H_4F_4O_2S$ requires C, 36·8; H, 1·8; F, 33·3%). Infrared absorption maxima at 3040, and 2980 cm.$^{-1}$ were ascribed to $\geqslant$C–H vibrations, at 1510 cm.$^{-1}$ to vibrations of a fluorinated benzene ring system, and at 1342 and 1158 cm.$^{-1}$ to two of the $>SO_2$ vibration modes.

Bis-(2,3,5,6-*tetrafluorophenyl*) *Disulphide.*—The tetrafluorothiophenol (2·7 g.) was oxidised with bromine [9] (*ca.* 1·1 mol.) in acetic acid (20 c.c.) as previously described. The gum (2·3 g.) left after evaporation of the acetic acid rapidly crystallised and was recrystallised twice from ethanol, to give the *disulphide* (0·5 g.), m. p. 38° (Found: C, 39·5; H, 0·5; F, 41·6. $C_{12}H_2F_8S_2$ requires C, 39·8; H, 0·6; F, 42·0%), $\nu_{max.}$ at 2900 ($\geqslant$C–H) and 1500 cm.$^{-1}$ (fluorinated benzene).

Action of Heat on Potassium 2,3,5,6-*Tetrafluorothiophenoxide.*—This compound (1·0 g.) was heated at 150—200° in a hard-glass test-tube for 10 min. and then allowed to cool. Water was added to the solid mass, and the mixture boiled and filtered; the filtrate gave a strongly positive cerous nitrate test for fluoride. The insoluble material (0·5 g.), softening at 150—160°, could not be crystallised and did not sublime at 200°/0·5 mm. The infrared spectrum, whilst containing absorption peaks associated with a fluorinated aromatic ring at 1500 cm.$^{-1}$, was different from that of the polymer formed from potassium pentafluorothiophenoxide.

We thank Dr. J. K. Brown for his advice on the infrared spectroscopy and the University for a scholarship (to P. R.).

THE UNIVERSITY, EDGBASTON, BIRMINGHAM, 15. [*Received, May 12th,* 1960.]