691. *Aromatic Polyfluoro-compounds. Part XIII.*[1] *Derivatives of Penta- and 2,3,5,6-Tetra-fluorothiophenol.*

By P. Robson, T. A. Smith, R. Stephens, and J. C. Tatlow.

A series of partly fluorinated aromatic sulphides has been prepared by condensation processes, and their structures have been established by desulphurisation. The susceptibility of fluoro-aromatic sulphur compounds to nucleophilic attack, and the orientation of some of the products, have been established. Pentafluoro-, 2,3,5,6-tetrafluoro-, and 4-acetamido-2,3,5,6-tetrafluoro-benzenesulphonyl chloride and a series of derivatives are described.

This paper describes extensions to our work on fluoro-aromatic sulphur compounds. The pentafluorothiophenoxide ion has been shown to be a nucleophile giving a polymer from hexafluorobenzene.[2] Pentafluorothiophenol is resistant to nucleophilic attack and a dithiol has not, so far, been made from it by reaction with sodium sulphide. It was either recovered, or, under conditions similar to those that gave tetrachlorobenzene-1,2-dithiol from pentachlorothiophenol,[3] afforded a perfluoropoly(phenylene sulphide). In the present work the fluoro-aromatic sulphide systems were prepared by multiple nucleophilic attack, reactants being chosen which prevent the building up of polymer chains, as in the earlier preparation of phenyl 2,3,5,6-tetrafluorophenyl sulphide from potassium thiophenoxide and pentafluorobenzene.[2] Reactions (i)—(vi) have now been investigated and the structures of the products established.

(In the reactions here depicted of polyfluorobenzene derivatives, hydrogen attached to a ring is numbered instead of the fluorine substituents.)

(i) $\mathrm{PhSK + C_6F_6 \longrightarrow \underset{(I)}{C_6F_4(SPh)_2\text{-}1,4} \longrightarrow \underset{(II)}{1\text{-}F{\cdot}C_6(SPh)_4{\cdot}F\text{-}4}}$

(ii) $\mathrm{4\text{-}H{\cdot}C_6F_4{\cdot}SK + C_6F_6 \longrightarrow 1,4\text{-}(4'\text{-}H{\cdot}C_6F_4{\cdot}S)_2C_6F_4}$ (III)

(iii) $\mathrm{4\text{-}H{\cdot}C_6F_4{\cdot}SK + 1,2,4\text{-}C_6H_3Cl(NO_2)_2 \longrightarrow 4\text{-}H{\cdot}C_6F_4{\cdot}S{\cdot}C_6H_3(NO_2)_2\text{-}2',4'}$ (IV)

(iv) $\mathrm{4\text{-}H{\cdot}C_6F_4{\cdot}SK + C_6HF_5 \longrightarrow 4\text{-}H{\cdot}C_6F_4{\cdot}S{\cdot}C_6F_4{\cdot}H\text{-}4'}$ (V)

(v) $\mathrm{\mathit{o}\text{-}NH_2{\cdot}C_6H_4{\cdot}SK + C_6HF_5 \longrightarrow 4\text{-}H{\cdot}C_6F_4{\cdot}S{\cdot}C_6H_4{\cdot}NH_2\text{-}\mathit{o}}$ (VI)

(vi) $\mathrm{2\mathit{o}\text{-}NH_2{\cdot}C_6H_4{\cdot}SK + C_6F_6 \longrightarrow 1,4\text{-}(\mathit{o}\text{-}NH_2{\cdot}C_6H_4{\cdot}S)_2C_6F_4}$ (VII)

The formation of the tetrakis-sulphide (II) as well as of the bis-sulphide (I) parallels the reaction of hexachlorobenzene with potassium thiophenoxide,[4] which gives 1,4-dichlorotetrakisthiophenylbenzene. With each of the sulphides [except (IV) where only one can be formed] structural allocation was carried out by desulphurisation with Raney nickel,[2] the products being isolated by gas chromatography. The 1,4-bis-sulphide (I) gave 1,2,4,5-tetrafluorobenzene[5] and benzene in the ratio of 1 : 2; the tetrakis-sulphide (II) gave *p*-difluorobenzene and benzene in the ratio of 1 : 4; the bis-sulphides (III) and (VII) and the monosulphide (VI) gave 1,2,4,5-tetrafluorobenzene. In every fluorine replacement [except the formation of compound (II)] the sulphide nucleophile attacked the *para*-position, in agreement with previous experience.[2,6] The attacks on pentafluorobenzene [reactions (iv) and (v)] confirm earlier results; in the formation of compounds (I), (III), and (VII) the second attack on the intermediate sulphide must be on the analogous position. Thus, compounds of the type $\mathrm{ArS{\cdot}C_6F_5}$ are attacked by nucleophiles at position 4 (where ArS = 1). It was of interest that in reaction (ii), even with a large excess of

---

[1] Part XII, Brooke, Burdon, and Tatlow, *J.*, 1962, 3253.
[2] Robson, Stacey, Stephens, and Tatlow, *J.*, 1960, 4754.
[3] Pikl, U.S.P. 2,842,578/1958.
[4] Kulka, *J. Org. Chem.*, 1959, **24**, 235.
[5] Finger, Reed, Burness, Fort, and Blough, *J. Amer. Chem. Soc.*, 1951, **73**, 145.
[6] Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768, and unpublished work.

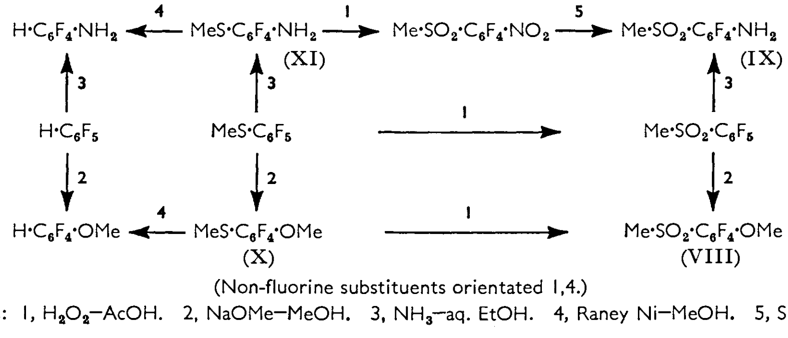
potassium 2,3,5,6-tetrafluorothiophenoxide, further substitution, as in (i), did not occur; this may be due to the weaker nucleophilic character of $H{\cdot}C_6F_4{\cdot}S^-$ and/or steric compression which might arise in the transition-state complex.

An attempted preparation of 1,3,4-trifluorophenothiazine by intramolecular nucleophilic displacement of the 2-fluorine atom of 2′-amino-2,3,5,6-tetrafluorodiphenyl sulphide by the amino-group was unsuccessful: from the deep red glassy product an intractable solid was isolated with spectroscopic properties consistent with those of a phenothiazine system, but this could not be purified.

Phenyl 2,3,5,6-tetrafluorophenyl sulphide was readily oxidised to the sulphone with hydrogen peroxide in acetic acid.[2] 1,2,4,5-tetrafluorobisphenylthiobenzene (I) and 1,4-difluoro-tetrakisthiophenylbenzene (II) gave sulphones under similar conditions. The very high-melting and comparatively insoluble 1,4-difluorotetrakisphenylsulphonylbenzene was not obtained pure. The more highly fluorinated sulphides (III and V) were not oxidised under these conditions, however, and this effect is believed to arise from the lower availability of the non-bonding electrons on the sulphur atom produced by the electronegative fluorobenzene nuclei.[2] A lower co-ordinating power has been reported for the sulphur in bistrifluoromethyl disulphide.[7]

Nucleophilic replacement of fluorine occurs readily with methyl pentafluorophenyl sulphide and sulphone and with sodium pentafluorobenzenesulphonate. The reaction of the last with cyanide ion can be explosive.[8] However, a fluorine replacement was here indicated in that sodium methoxide in methanol gave a tetrafluoromethoxybenzenesulphonic acid. Unfortunately the orientation of this acid could not be established since an attempted synthesis, the reaction of 2,3,5,6-tetrafluoroanisole with stabilised sulphur trioxide (normally a sulphonating agent), gave 2,3,5,6-tetrafluorophenol. This suggests an alternative demethylation agent to aluminium chloride which is known to react with a wide variety of fluoro-compounds.[9]

The position of the fluorine that was replaced in the reactions of methyl pentafluorophenyl sulphone and sulphide was determined. The sulphone reacted readily with sodium methoxide in methanol and with ammonia in aqueous ethanol to give, respectively, the 4-methoxy- and the 4-amino-sulphone (VIII and IX). These structures were established by preparing the corresponding sulphides (X and XI) by the same procedure. When oxidised, these afforded the above sulphones (VIII and IX). The sulphides were orientated by desulphurisation to known compounds, 2,3,5,6-tetrafluoroanisole[10] and 2,3,5,6-tetrafluoroaniline[1] as depicted in the annexed scheme.



(Non-fluorine substituents orientated 1,4.)

Reagents: 1, H_2O_2–AcOH. 2, NaOMe–MeOH. 3, NH_3–aq. EtOH. 4, Raney Ni–MeOH. 5, Sn–HCl.

The obvious routes to pentafluorobenzenesulphonyl chloride, reaction of pentafluorobenzenesulphonic acid[8] or its sodium salt, with phosphorus pentachloride or thionyl

---

[7] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2549.

[8] Nield, Stephens, and Tatlow, *J.*, 1959, 166.

[9] Henne and Newman, *J. Amer. Chem. Soc.*, 1938, **60**, 1697; Gething, Patrick, Smith, and Tatlow, *J.*, 1962, 190.

[10] Nield, Stephens, and Tatlow, *J.*, 1960, 3800.

chloride failed. However, oxidation of penta- and of 2,3,5,6-tetra-fluorothiophenol with chlorine and hydrogen peroxide in acetic acid gave good yields of the sulphonyl chlorides, which distilled without decomposition. The normal procedure[11] for this oxidation involves chlorine, acetic acid, and the correct proportion of water to afford the fully oxidised state of the sulphur. It was applied successfully to the preparation of trifluoromethanesulphonyl chloride.[12] However, in the present case it gave an impure product, believed to be contaminated by sulphenyl and sulphinyl chlorides, a consequence, perhaps, of a lower co-ordinating power of the sulphur in these highly fluorinated systems. The reaction probably largely follows the sequence:

$$C_6F_5{\cdot}SH \longrightarrow C_6F_5{\cdot}S{\cdot}S{\cdot}C_6F_5 \longrightarrow C_6F_5{\cdot}SCl \longrightarrow C_6F_5{\cdot}SOCl \longrightarrow C_6F_5{\cdot}SO_2Cl$$

It is known[12] that trifluoromethanesulphenyl chloride is oxidised by hydrogen peroxide to trifluoromethanesulphonyl chloride. The polyfluorobenzenesulphonyl chlorides were both high-boiling colourless liquids which were easily hydrolysed to the acids by water in pyridine solution. Pentafluorobenzenesulphonyl chloride was slowly hydrolysed by aqueous alkali at 18°, and by boiling water, to the sulphonic acid with no noticeable loss of fluoride ion.

The structure of 2,3,5,6-tetrafluorobenzenesulphonic acid was confirmed, since the material made by hydrolysis of the sulphonyl chloride and that obtained from the sulphonation of 1,2,4,5-tetrafluorobenzene with stabilised sulphur trioxide formed identical *S*-benzylthiouronium and potassium salts. Further, the first of these salts was different from those obtained from the acids obtained on sulphonation of 1,2,3,5- and of 1,2,3,4-tetrafluorobenzene. This substantiates the orientation of 2,3,5,6-tetrafluorothiophenol originally based on its desulphurisation by Raney nickel.[2]

Penta- and 2,3,5,6-tetra-fluorobenzenesulphonyl chloride were fully characterised: the former with aniline and phenol gave pentafluorobenzenesulphonanilide and phenyl pentafluorobenzenesulphonate, respectively, and the latter with aniline, phenol, and pentafluorophenol gave 2,3,5,6-tetrafluorobenzenesulphonanilide and phenyl and pentafluorophenyl 2,3,5,6-tetrafluorobenzenesulphonate, respectively. All these condensations were effected under Schotten–Baumann reaction conditions: attempted condensations in pyridine gave no tractable product; this result is probably related to the known reactivity of pyridine towards fluoro-aromatics[2] and fluoro-olefins.[13]

Penta- and 2,3,5,6-tetra-fluorobenzenesulphonyl chloride reacted readily with ammonia, but in addition to the expected sulphonamides (XII and XIV), substantial amounts of the ammonium salts of the disulphonimides (XIII and XV) were obtained. This parallels

$$\begin{aligned} C_6F_5{\cdot}SO_2Cl + NH_3 &\longrightarrow C_6F_5{\cdot}SO_2{\cdot}NH_2 \text{ (XII)} \\ 2C_6F_5{\cdot}SO_2Cl + 2NH_3 &\longrightarrow NH_4^{+}\,{}^{-}N(SO_2{\cdot}C_6F_5)_2 \text{ (XIII)} \\ 4\text{-}H{\cdot}C_6F_4{\cdot}SO_2Cl + NH_3 &\longrightarrow 4\text{-}H{\cdot}C_6F_4{\cdot}SO_2{\cdot}NH_2 \text{ (XIV)} \\ 2\text{-}(4\text{-}H{\cdot}C_6F_4{\cdot}SO_2Cl) + 2NH_3 &\longrightarrow NH_4^{+}\,{}^{-}N(SO_2{\cdot}C_6F_4{\cdot}H\text{-}4)_2 \text{ (XV)} \end{aligned}$$

the reaction of ammonia with highly chlorinated benzenesulphonyl chlorides.[14] However, pentafluorobenzenesulphonamide did not condense with pentafluorobenzenesulphonyl chloride. The free imides were readily prepared by treatment of the ammonium salt with a cation-exchange resin in water.

Pentafluorobenzenesulphonamide was found to be less susceptible to nucleophilic replacement than methyl pentafluorophenyl sulphide and sulphone, probably because the acidity of the amine group gives an anion in the presence of a base such as sodium methoxide or ammonia and consequently deactivates the nuclear fluorine to nucleophilic attack. Thus, although a tetrafluoromethoxybenzenesulphonamide could be prepared,

---

[11] Lee and Dougherty, *J. Org. Chem.*, 1940, **5**, 81.

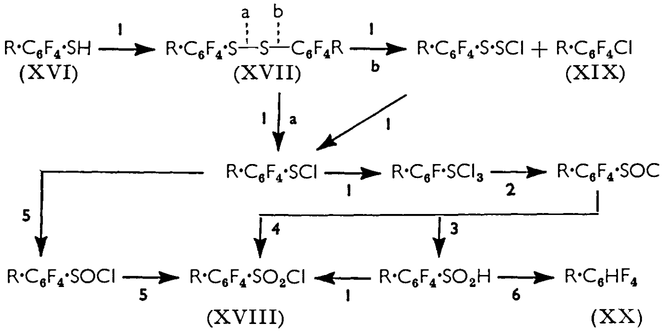
[12] Haszeldine and Kidd, *J.*, 1955, 2901.

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

[14] Farrer, *J.*, 1960, 3063.

ethanolic aqueous ammonia did not react with pentafluorobenzenesulphonamide at 200°. However, with sodamide in liquid ammonia replacement of the *para*-fluorine atom occurred, to give 4-aminotetrafluorobenzenesulphonamide in small yield. Whilst there was no chemical method available for establishing the orientation of the tetrafluoromethoxybenzenesulphonamide, an alternative synthesis of 4-aminotetrafluorobenzenesulphonamide established its structure and also provided a general route to amides of tetrafluorosulphanilic acid. It has been shown [6] that pentafluoroaniline reacts slowly with nucleophiles to produce *meta*-substituted products. However, pentafluoroacetanilide reacted vigorously with sodium hydrogen sulphide in dimethyl formamide, to give a high yield of 4-acetamido-2,3,5,6-tetrafluorothiophenol (XVI) which was desulphurised by Raney nickel to the known 2,3,5,6-tetrafluoroacetanilide [1] (XX), showing clearly a *para*-directional influence in this replacement. The thiol was characterised as 4-acetamido-2,3,5,6-tetrafluoro-2′,4′-dinitrodiphenyl sulphide, the disulphide (XVII), and the sulphonyl chloride (XVIII); it was deacetylated, to give the crystalline 4-aminotetrafluorothiophenol.

4-Acetamidotetrafluorobenzenesulphonyl chloride was prepared from the thiol with chlorine in acetic acid containing the amount of water calculated for formation of the sulphone group. The initial precipitate of the high-melting disulphide (XVII) slowly dissolved and the sulphonyl chloride (XVIII) was obtained crystalline. Surprisingly, however, it was accompanied by substantial amounts of the known 2,3,5,6-tetrafluoroacetanilide (XX) and smaller variable quantities of a chlorotetrafluoroacetanilide (XIX), presumably 4-chlorotetrafluoroacetanilide; use of hydrogen peroxide in place of water did not substantially affect this result. It was readily shown that 4-acetamidotetrafluorobenzenesulphonyl chloride does not give the above by-products under the conditions of its formation. They must, therefore, arise from alternative processes in what is undoubtedly a complex reaction.[15] Probable pathways are represented in the Scheme.



R = NHAc. Non-fluorine substituents are orientated 1,4.

Reagents: 1, Cl_2. 2, AcOH. 3, H_2O. 4, Cl_2–AcOH. 5, H_2O_2 or Cl_2–H_2O. 6, –SO_2.

None of the unnumbered intermediates was isolated but evidence [15] is available for the formation of these types of compounds under such conditions. Loss of sulphur dioxide from the sulphinic acid may well be easy since 2,4-dinitrobenzenesulphinic acid, prepared [16] by the hydrolysis of the sulphenyl chloride in acetic acid at 15°, and related sulphinic acids [18] appear to lose sulphur dioxide spontaneously at 15°. Unsymmetrical cleavage of a disulphide (cf. XVII) has been reported.[19]

---

[15] Douglass, Farah, and Thomas, *J. Org. Chem.*, 1961, 1996.

[16] Kharasch, King, and Bruice, *J. Amer. Chem. Soc.*, 1955, **77**, 931.

[17] Stephens and Tatlow, *Chem. and Ind.*, 1957, 821; Richardson, Ph.D. Thesis, University of Birmingham, 1958, p. 98.

[18] Bradbury and Smith, *J.*, 1952, 2943; Davies, Storrie, and Tucker, *J.*, 1931, 624; Dann and Davies, *J.*, 1929, 1050.

[19] Schulze, Short, and Crouch, *Ind. Eng. Chem.*, 1950, **42**, 916.

4-Acetamidotetrafluorobenzenesulphonyl chloride (XVIII) reacted readily with ammonia at 16° to give the sulphonamide; there was no evidence of imide formation. The acetamido-sulphonamide was hydrolysed with mineral acid to 4-aminotetrafluorobenzenesulphonamide, which was identical with the product from pentafluorobenzenesulphonamide and sodamide in liquid ammonia.

As with penta- and 2,3,5,6-tetra-fluorobenzenesulphonyl chloride, pyridine could not be used as solvent in condensation reactions of the sulphonyl chloride, intractable tars being produced. The use of Schotten–Baumann conditions also gave tars. However, the sulphonyl chloride and aniline in benzene gave an anilide which was hydrolysed by dilute mineral acid to 4-aminotetrafluorobenzenesulphonanilide.

The biological activity of several of the compounds described is being examined. Preliminary results indicate a very low activity for 4-aminotetrafluorobenzenesulphonamide against *Staphylococcus aureus*, *Streptococcus pyogenes*, *Klebsiella aerogenes*, and *Escherichia coli*.

EXPERIMENTAL

Ultraviolet data refer to EtOH solutions.

Penta- and 2,3,5,6-tetrafluorothiophenol were prepared from hexa- and penta-fluorobenzene, respectively, with sodium hydrogen sulphide in pyridine.[2]

Attempted Preparation of a Tetrafluorobenzenedithiol.—(*a*) Hydrogen sulphide was bubbled through a hot solution of sodium hydroxide (12·2 g.) in ethylene glycol (20 c.c.) for 3 hr., and the resulting liquid was quickly added to a cooled, stirred solution of hexafluorobenzene (10 g.) in pyridine (70 c.c.). After the initial vigorous reaction, the mixture was heated in a stainless-steel autoclave at 200° for 16 hr; this gave a perfluoropoly(phenylene sulphide) (10·2 g.), m. p. $>300°$, of the type previously [2] obtained.

(*b*) A hot solution of sodium hydrogen sulphide (12·4 g.), prepared as described above, was quickly added to a cooled stirred solution of pentafluorothiophenol (10 g.) in pyridine (70 c.c.). The mixture was heated under reflux for 5 min.; this gave pentafluorothiophenol (7·5 g.), b. p. 142° (lit.,[2] 143°), with a correct infrared spectrum.

1,2,4,5-*Tetrafluorobisphenylthiobenzene.*—Hexafluorobenzene (5·0 g.) in pyridine (20 c.c.) was added dropwise to a refluxing solution of potassium thiophenoxide (8·0 g.) in pyridine (40 c.c.). After 10 minutes' refluxing the mixture was poured on ice (*ca.* 100 g.), acidified with 8N-hydrochloric acid, and extracted with ether. The dried ($MgSO_4$) extracts were evaporated, to give the *bis-sulphide* (5·4 g.), m. p. 110—111° (Found: C, 59·4; H, 2·7; F, 20·8. $C_{18}H_{10}F_4S_2$ requires C, 59·0; H, 2·7; F, 20·7%), $\nu_{max.}$ 1480 (non-fluorinated benzene ring), 1490 (fluorinated benzene ring), and 746 cm.$^{-1}$ ($\geqq$C·S), $\lambda_{max.}$ 2920 Å (ε 1·38 × 10^4).

A mixture of the sulphide (0·5 g.), acetic acid (10 c.c.), and 30% w/v hydrogen peroxide (1·0 c.c.) was kept at 100° for 1 hr. The white precipitate (0·5 g.) obtained on pouring the mixture into water was collected and recrystallised from acetic acid, to give 2,3,5,6-*tetrafluorobisphenylsulphonylbenzene*, m. p. 285° (Found: C, 50·2; H, 2·3; F, 18·1. $C_{18}H_{10}F_4O_4S_2$ requires C, 50·2; H, 2·3; F, 17·7%), $\lambda_{max.}$ (saturated soln.) 2520 Å, $\nu_{max.}$ 1490 and 1480 (benzene rings), 1164 and 1351 cm.$^{-1}$ (SO_2).

The sulphide (3·0 g.) was added to a suspension of Raney nickel (grade W4; 25 g.) in butan-1-ol (200 c.c.) and, after 5 hours' refluxing, the mixture was distilled through a 2′ vacuum-jacketed column packed with Dixon gauze rings (1/16″ × 1/16″), to give a fraction (4·9 g.), b. p. 66·7—100°, which was shown by analytical gas chromatography to contain 5 components; separation of the mixture (4·3 g.) by preparative-scale gas chromatography (90°, N_2 12 l./hr.) gave a fraction (0·7 g.) which was shown by infrared spectroscopy (i.r.) to be a 1 : 2 mixture of 1,2,4,5-tetrafluorobenzene and benzene. No other aromatic compound was obtained.

1,4-*Difluorotetrakisphenylthiobenzene.*—Hexafluorobenzene (1·5 g.) in pyridine was added slowly to a refluxing solution of potassium thiophenoxide (5·4 g.) in pyridine (20 c.c.), and the mixture refluxed for 25 min., poured on ice (50 g.), and acidified with 8N-hydrochloric acid. The yellow precipitate (4·5 g.) was collected and recrystallised from benzene, to give the *tetrakis-sulphide* (2·3 g.), m. p. 142—144° (Found: C, 65·6; H, 3·7; F, 7·3. $C_{30}H_{20}F_2S_4$ requires C, 65·9; H, 3·7; F, 6·9%), i.r. peaks at 1497, 1493, and 737 cm.$^{-1}$ were ascribed to vibrational modes of the non-fluorinated benzene ring, the fluorinated benzene ring, and the C–S bond, respectvely. In n-hexane it had $\lambda_{max.}$ 2480 (ε 3·54 × 10^4) and 2500 Å (ε 3·5 × 10^4).

A mixture of the tetrakis-sulphide (0·13 g.), 30% hydrogen peroxide (1 c.c.), and acetic acid (10 c.c.) was refluxed for 1¼ hr., then poured into water (50 c.c.), and the precipitate (0·1 g.) was collected and recrystallised from aqueous acetic acid, to give the believed 1,4-*difluorotetrakisphenylsulphonylbenzene* (0·05 g.), m. p. 303—305° (Found: C, 54·2; H, 2·9; S, 20·6. $C_{30}H_{20}F_2O_8S_4$ requires C, 53·3; H, 3·0; S, 19·0%), $\lambda_{max.}$ (saturated soln.) 2520 Å.

The tetrakis-sulphide (2·1 g.) and Raney nickel (grade W4; 25 g.) in butan-1-ol (200 c.c.) gave in the usual way, a major component (0·4 g.) shown (i.r.) to contain benzene and *p*-difluorobenzene in the ratio of 4 : 1. No other aromatic compound was obtained.

2,3,5,6-*Tetrafluoro*-2′,4′-*dinitrodiphenyl Sulphide*.—Potassium tetrafluorothiophenoxide (0·27 g.) (prepared from 2,3,5,6-tetrafluorothiophenol [2]), chloro-2,4-dinitrobenzene (0·5 g.), and ethanol (20 c.c.) were refluxed for 10 min., then cooled, giving a crystalline precipitate. Recrystallisation from chloroform–ethyl acetate gave the *sulphide* (0·20 g.), m. p. 180—182° (Found: C, 41·6; H, 1·6. $C_{12}H_4F_4N_2O_4S$ requires C, 41·4; H, 1·2%).

2,3,5,6-*Tetrafluorobis*-(2,3,5,6-*tetrafluorophenylthio*)*benzene*.—Hexafluorobenzene (2·14 g.) in pyridine (20 c.c.) was added to a refluxing solution of potassium 2,3,5,6-tetrafluorothiophenoxide [2] (4·75 g.) in pyridine (50 c.c.), and after 35 minutes' refluxing the mixture was poured on ice (100 g.). Acidification with 16N-hydrochloric acid and ether-extraction gave a solid (4·1 g.) which recrystallised from light petroleum (b. p. 80—100°) to give 2,3,5,6-*tetrafluorobis*-(2,3,5,6-*tetrafluorophenylthio*)-*benzene* (3·0 g.), m. p. 157° (Found: C, 42·3; H, 0·3. $C_{18}H_2F_{12}S_2$ requires C, 42·4; H, 0·4%), $\nu_{max.}$ 3020 ($\geqslant$CH), 1495 (fluorinated benzene ring), and 714 cm.$^{-1}$ (C–S), $\lambda_{max.}$ 2820 Å (ε 1·67 × 10^4).

When hexafluorobenzene (0·2 mole, 0·69 g.) in pyridine was added very slowly to a refluxing mixture of potassium 2,3,5,6-tetrafluorothiophenoxide (1 mole, 3·4 g.) and pyridine (20 c.c.) and then refluxed for 6 hr., the same isolation procedure gave 2,3,5,6-tetrafluorobis-(2,3,5,6-tetrafluorophenylthio)benzene (1·5 g.), m. p. and mixed m. p. 157°, and 2,3,5,6-tetrafluorothiophenol (0·9 g.), b. p. 147° (correct i.r. spectrum).

A solution of 2,3,5,6-tetrafluorobis-(2,3,5,6-tetrafluorophenylthio)benzene (0·3 g.) in acetic acid (10 c.c.) containing 30% hydrogen peroxide (1 c.c.) was kept at 100° for 1 hr. and then poured into water (50 c.c.). The crystalline precipitate (0·23 g.) had m. p. 153°, alone and in admixture with the starting material; the i.r. and ultraviolet (u.v.) spectra were identical with those of the starting material.

Desulphurisation of 2,3,5,6-*Tetrafluorobis*-(2,3,5,6-*tetrafluorophenylthio*)*benzene*.—The sulphide (2·03 g.) and Raney nickel (grade W4; 25 g.) in butan-1-ol (200 c.c.) gave, in the usual way, 1,2,4,5-tetrafluorobenzene (1·3 g.) as the main fraction (correct i.r. spectrum). No other aromatic compound was present.

Bis-(2,3,5,6-*tetrafluorophenyl*) *Sulphide*.—Pentafluorobenzene (3·87 g.) in pyridine (30 c.c.) was slowly added to a refluxing solution of potassium 2,3,5,6-tetrafluorothiophenoxide [2] (5·05 g.) in pyridine (50 c.c.). After 30 minutes' refluxing, the mixture was poured on ice (150 g.) and acidified with 16N-hydrochloric acid. The dried ($MgSO_4$) ether extracts of the resulting solution were evaporated and the residue distilled, to give 2,3,5,6-tetrafluorothiophenol (1·71 g.), b. p. 147°, and *bis*-(2,3,5,6-*tetrafluorophenyl*) *sulphide* (2·16 g.), b. p. 82°/0·35 mm., m. p. 44·5° (Found: C, 43·9; H, 0·6. $C_{12}H_2F_8S$ requires C, 43·6; H, 0·6%), $\nu_{max.}$ 3120 ($\geqslant$CH), 1500 (fluorinated benzene ring), and 727 cm.$^{-1}$ (C–S bond), $\lambda_{max.}$ 2620 (ε 1·94 × 10^3) and 2680 Å (ε 2·01 × 10^3).

The sulphide (0·1 g.), acetic acid (2·5 c.c.), and 30% hydrogen peroxide (0·5 c.c.) were refluxed for 2 hr., then poured into water (25 c.c.), to give an oily precipitate which at 0° gave crystals (0·025 g.) m. p. 28°, alone or mixed with the starting material and with the same i.r. spectrum.

The sulphide (2·0 g.) and nickel (grade W4; 25 g.) in butan-1-ol (200 c.c.), in the previous way, gave 1,2,4,5-tetrafluorobenzene (0·5 g.) as the only aromatic compound (correct i.r. spectrum).

2′-*Amino*-2,3,5,6-*tetrafluorodiphenyl Sulphide*.—A hot solution of *o*-aminothiophenol (7·4 g.) and sodium hydroxide (2·86 g.) in ethylene glycol (20 c.c.) was quickly added to a boiling solution of pentafluorobenzene (10 g.) in pyridine (60 c.c.). After 30 minutes' refluxing, the mixture was poured on ice (80 g.), acidified with 8N-hydrochloric acid, and extracted with ether. Evaporation of the dried ($MgSO_4$) ether solution, followed by distillation of the residue, gave a colourless solid (8·9 g.), b. p. 123·5/0·45 mm. Recrystallisation from light petroleum (b. p. 40—60°) gave 2′-*amino*-2,3,5,6-*tetrafluorodiphenyl sulphide*, m. p. 65·5—67° (Found: C, 52·8; H, 2·6; S, 12·0. $C_{12}H_7F_4NS$ requires C, 52·7; H, 2·6; S, 11·7%), $\nu_{max.}$ 3460 and 3375 (NH_2), 1490 (fluorinated benzene ring), 1452 (benzene ring), and 712 cm.$^{-1}$ (C–S), $\lambda_{max.}$ 3105 (ε 3·65 × 10^3) and 3115 Å (ε 3·65 × 10^3).

A mixture of the sulphide (0·24 g.), 12% aqueous sodium hydroxide (5 c.c.), and benzoyl chloride (0·14 c.c.) was shaken for 30 min., then poured into water (30 c.c.). The precipitate was washed, dried, and recrystallised from ethanol, to give 2′-*benzamidotetrafluorodiphenyl sulphide* (0·28 g.), m. p. 157·5—158·5° (Found: C, 60·3; H, 3·0. $C_{19}H_{11}F_4NOS$ requires C, 60·5; H, 2·9%).

The amino-sulphide (1·56 g.) and Raney nickel (grade W4; 12 g.) in butan-1-ol (45 c.c.) gave, in the usual way, 1,2,4,5-tetrafluorobenzene 0·5 g. (correct i.r. spectrum). No other aromatic was obtained. No attempt was made to isolate aniline.

Attempted Preparation of 1,2,4-*Trifluorophenothiazine*.—2′-Amino-2,3,5,6-tetrafluorodiphenyl sulphide (5·0 g.), anhydrous potassium carbonate (2·75 g.), copper bronze (0·35 g.), and dimethylformamide (80 c.c.) were refluxed and stirred in an atmosphere of dry nitrogen for 6½ hr., then filtered hot; the solid was washed with dimethylformamide (20 c.c.). The combined filtrate and washings were poured into water (1½ l.) and, after 16 hr., filtered. The solid was washed with water and dried. A benzene solution of the solid was chromatographed on alumina (Brockmann activity 1) to give a deep red, glass-like solid and the suspected 1,2,4-trifluorophenothiazine (0·1 g.), m. p. 78—85°, which could not be purified. It had $\lambda_{max.}$ 2530 Å (ε 3·05 × 10^4) (phenothiazine, 2545 Å; ε 4·33 × 10^4). There were i.r. peaks at 3400 (>NH), 1630, and 1490 cm.$^{-1}$ (fluorinated benzene ring). The i.r. spectrum of phenothiazine was measured under identical conditions and was similar.

1,4-*Di*-(o-*Aminophenylthio*)*tetrafluorobenzene*.—A hot solution of *o*-aminothiophenol (13·5 g.) and sodium hydroxide (5·5 g.) in ethylene glycol (20 c.c.) was quickly added to a refluxing solution of hexafluorobenzene (10 g.) in pyridine (60 c.c.). After 30 minutes' refluxing the mixture was cooled, poured on ice (100 g.), acidified with 8N-hydrochloric acid, and extracted with ether. Evaporation of the ether left a solid which recrystallised from light petroleum (b. p. 80—100°), to give 1,4-*di*-(o-*aminothiophenyl*)*tetrafluorobenzene* (5·0 g.), m. p. 134—135° (Found: C, 54·2; H, 3·0; S, 16·4. $C_{18}H_{12}F_4N_2S_2$ requires C, 54·5; H, 3·0; S, 16·2%), $\nu_{max.}$ 3450 and 3350 cm.$^{-1}$ (NH_2), $\lambda_{max.}$ 2750 (ε 1·33 × 10^4) and 3125 Å (ε 8·29 × 10^3).

A mixture of the sulphide (0·2 g.), 12% aqueous sodium hydroxide solution (5 c.c.), and benzoyl chloride (0·16 g.) was shaken for 1½ hr. and water then added. The precipitate recrystallised from ethanol to give 1,4-*di*-(o-*benzamidophenylthio*)*tetrafluorobenzene* (0·21 g.), m. p. 226—228° (Found: C, 62·9; H, 3·3. $C_{32}H_{20}F_4N_2O_2S_2$ requires C, 63·6; H, 3·3%).

The amino-sulphide (2·7 g.) and Raney nickel (grade W4; 25 g.) in butan-1-ol (200 c.c.), in the usual sequence, gave 1,2,4,5-tetrafluorobenzene (0·4 g.) (correct i.r. spectrum). No other aromatic compound was obtained. No attempt was made to isolate aniline.

Methyl Tetrafluoro-4-*methoxyphenyl Sulphone*.—Methyl pentafluorophenyl sulphone [2] (0·40 g.), sodium (0·04 g.), and dry (Mg) methyl alcohol (8 c.c.) were refluxed for 1½ hr. Addition to water (50 c.c.) gave a white solid (0·37 g.) which recrystallised from aqueous ethanol to give *methyl* 2,3,5,6-*tetrafluoro*-4-*methoxyphenyl sulphone* (0·3 g.), m. p. 75° (Found: C, 37·4; H, 2·3; F, 29·0. $C_8H_6F_4O_3S$ requires C, 37·2; H, 2·3; F, 29·4%), $\lambda_{max.}$ 2690 Å (ε 1·35 × 10^3).

Methyl Tetrafluoro-4-*methoxyphenyl Sulphide*.—Methyl pentafluorophenyl sulphide [2] (4·0 g.), sodium (0·88 g.), and dry (Mg) methanol (40 c.c.) were refluxed for 21½ hr. and then poured into water (150 c.c.). The liquid precipitated was extracted with ether and distilled, to give the *methoxy-sulphide* (3·6 g.) b. p. 118°/15 mm. (Found: C, 42·7; H, 2·6; S, 14·2. $C_8H_6F_4OS$ requires C, 42·5; H, 2·7; S, 14·2%), $\lambda_{max.}$ 2640 Å (ε 6·90 × 10^3).

A mixture of the sulphide (0·57 g.), 30% hydrogen peroxide (5 c.c.), and acetic acid (10 c.c.) were kept at 100° for 2½ hr., then poured into water. The crystals obtained recrystallised from aqueous ethanol to give the sulphone (0·35 g.), m. p. and mixed m. p. 75° (i.r. spectra identical).

The methoxysulphide (2·3 g.) was quickly added to a suspension of Raney nickel (grade W4; 20 g.) in methanol (150 c.c.). After 6 hours' refluxing, the nickel was removed and washed with methanol. The filtrate and washings were distilled through a 1′ Vigreux column to give 2,3,5,6-tetrafluoroanisole [17] (0·5 g.), b. p. 145° (correct i.r. spectrum). The positions of the fluorine atoms were established by nuclear magnetic resonance spectroscopy; only two magnetically different kinds of fluorine atoms were present.

4-*Aminotetrafluorophenyl Methyl Sulphone.*—Methyl pentafluorophenyl sulphone (0·45 g.), aqueous ammonia (*d* 0·88; 15 c.c.), and ethanol (15 c.c.) were kept at 15° for 16 hr., then added to an excess of dilute sodium hydroxide solution and extracted with ether. The extracts (3 × 50 c.c.) were dried ($MgSO_4$), filtered, and evaporated, leaving a solid (0·37 g.) which recrystallised from water to give the 4-*amino-sulphone* (0·07 g.), m. p. 169° (Found: C, 34·6; H, 2·3; F, 31·3. $C_7H_5F_4O_2NS$ requires C, 34·6; H, 2·1; F, 31·2%), $\lambda_{max.}$ 2670 Å (ε 1·49 × 10^4), $\nu_{max.}$ 3380 and 3275 (NH_2), 1491 (fluorinated benzene ring), and 1326 and 1150 cm.$^{-1}$ ($>SO_2$).

4-*Aminotetrafluorophenyl Methyl Sulphide.*—Methyl pentafluorophenyl sulphide (4·16 g.), aqueous ammonia (*d* 0·88; 11 c.c.), and ethanol (15 c.c.) were kept in a sealed tube at 150° for 14½ hr., then added to an excess of dilute sodium hydroxide solution and extracted with ether. Evaporation of the ether left a solid which was recrystallised from light petroleum (b. p. 40—60°), to give the *amino-sulphide* (2·3 g.), m. p. 82·5—83·5° (Found: C, 39·7; H, 2·3; F, 35·9. $C_7H_5F_4NS$ requires C, 39·8; H, 2·4; F, 36·0%), $\lambda_{max.}$ 2350 (ε 1·28 × 10^4) and 2630 Å (ε 1·49 × 10^4).

The sulphide (0·2 g.), 30% hydrogen peroxide (3·5 c.c.), and acetic acid (5 c.c.) were kept at 100° for 2½ hr., then poured into water, giving a solid. Recrystallisation from aqueous ethanol gave *methyl tetrafluoro-*4-*nitrophenyl sulphone* (0·1 g.), m. p. 137° (Found: C, 31·1; H, 1·1; F, 27·9. $C_7H_3F_4NO_4S$ requires C, 30·8; H, 1·1; F, 27·8%), $\lambda_{max.}$ 2975 Å (ε 3·72 × 10^3).

The nitro-compound (0·15 g.) was reduced with granulated tin (0·5 g.) and 16N-hydrochloric acid (5 c.c.) in the presence of ethanol (1 c.c.) for ½ hr. at 100°. The mixture was made alkaline with 10N-sodium hydroxide and extracted with ether. The ether extracts were dried ($MgSO_4$), filtered, and evaporated, to leave a solid (0·12 g.) which recrystallised from water to give 4-aminotetrafluorophenyl methyl sulphone (0·07 g.), m. p. 174° alone and in admixture with the compound obtained from the ammination of pentafluorophenyl methyl sulphone; their i.r. spectra were identical.

The amino-sulphide (1·9 g.) was desulphurised with Raney nickel (grade W4; 25 g.) in methanol (200 c.c.) in the previously described way, giving 2,3,5,6-tetrafluoroaniline (0·55 g.), b. p. 156° (correct i.r. spectrum [1,6]). With acetic anhydride and sulphuric acid it gave 2,3,5,6-tetrafluoroacetanilide, m. p. 140·5° alone and in admixture with an authentic specimen.[1,6]

A Tetrafluoromethoxybenzenesulphonic Acid.—Pentafluorobenzenesulphonic acid [8] (2·05 g.), sodium (0·41 g.), and dry (Mg) methanol (25 c.c.) were refluxed for 2¼ hr. and then the solvent was removed to leave a solid (1·8 g.) which was dissolved in water (10 c.c.). A portion (5 c.c.) of the aqueous solution was acidified to pH 4 with 4N-hydrochloric acid, and a saturated aqueous solution of *S*-benzylthiouronium chloride was added. The precipitate recrystallised from water to give an *S-benzylthiouronium tetrafluoromethoxybenzenesulphonate,* m. p. 121—122·5° (Found: C, 41·9; H, 3·5. $C_{15}H_{14}F_4N_2O_4S$ requires C, 42·2; H, 3·3%).

Demethylation of 2,3,5,6-*Tetrafluoroanisole.*—This compound (2·2 g.) and stabilised sulphur trioxide (14 g.) were kept at 15° for 24 hr., then concentrated sulphuric acid (20 c.c.) was added and the solution poured on ice (200 g.). The acid solution was extracted continuously with ether for 24 hr. and the dried ($MgSO_4$) extract was filtered and evaporated, to leave a brown liquid which distilled to give 2,3,5,6-tetrafluorophenol (1·0 g.), b. p. 140°, characterised as its toluene-*p*-sulphonate, m. p. 81—82° (lit.,[17] 82°) (Found: C, 49·1; H, 2·5. Calc. for $C_{13}H_8F_4O_3S$: C, 48·7; H, 2·5%).

Pentafluorobenzenesulphonyl Chloride.—Dry chlorine was briskly passed through a mixture of pentafluorothiophenol (11·2 g.), acetic acid (70 c.c.) and 80% w/v hydrogen peroxide (2·3 c.c.) for 2 hr. The mixture was then poured into water and extracted with ether (3 × 100 c.c.). The combined extracts were washed twice with saturated aqueous sodium metabisulphite, three times with saturated sodium hydrogen carbonate, and once with water. The dried ($MgSO_4$) ether extract was then filtered and evaporated, to leave a liquid which when distilled gave *pentafluorobenzenesulphonyl chloride* (9·0 g.), b. p. 210—211° (Found: C, 27·1; H, 0; F, 35·6. $C_6F_5ClO_2S$ requires C, 27·0; H, 0; F, 35·6%), $\nu_{max.}$ 1515 (fluorinated benzene ring), 1415 and 1195 cm.$^{-1}$ (SO_2), $\lambda_{max.}$ (in ethanol or n-hexane) 2735 Å (ε 2·30 × 10^3).

Pentafluorobenzenesulphonic Acid.—(*a*) Pentafluorobenzenesulphonyl chloride (1·2 g.), pyridine (20 c.c.), and water (5 c.c.) were kept at 18° for 24 hr. and then poured into 8N-hydrochloric acid (200 c.c.), and the solution was extracted continuously with ether for 15 hr. The dried ($MgSO_4$) extract was filtered and evaporated, to leave a partially crystalline residue (0·7 g.) which was dissolved in water (10 c.c.). The solution was divided into two portions.

One portion was adjusted to pH 4 and added to saturated aqueous *S*-benzylthiouronium chloride (20 c.c.). The precipitate (0·25 g.) was twice recrystallised from water, to give *S*-benzylthiouronium pentafluorobenzenesulphonate (0·18 g.) m. p. 177° alone or mixed with an authentic specimen[8] (Found: C, 40·8; H, 2·7. Calc. for $C_{14}H_{11}F_5N_2O_3S_2$: C, 40·6; H, 2·7%).

On addition of 50% w/w potassium hydroxide solution (20 c.c.) to the second portion, a crystalline precipitate was formed. Filtration and recrystallisation from water gave potassium pentafluorobenzenesulphonate (0·3 g.) with a correct i.r. spectrum (see below).

(*b*) Pentafluorobenzenesulphonyl chloride (0·9 g.), water (5 c.c.), and potassium hydroxide (0·32 g.) were shaken together for 15 hr. at 18°. The precipitate (1·1 g.) was twice recrystallised from water, to give *potassium pentafluorobenzenesulphonate* (0·4 g.) (Found: C, 25·2; H, 0·1; F, 33·5. $C_6F_5KO_3S$ requires C, 25·2; H, 0; F, 33·2%).

(*c*) Pentafluorobenzenesulphonyl chloride (1·27 g.) and water (5 c.c.) were kept at 100° for 4½ hr., then *S*-benzylthiouronium chloride solution was added, giving *S*-benzylthiouronium pentafluorobenzenesulphonate (1·7 g.), m. p. 176·5—177·5°.

The sulphonyl chloride (0·3 g.), aniline (0·1 g.), water (5 c.c.), and sodium hydroxide (0·1 g.) were shaken together at 16° for 2½ hr., then poured into water (10 c.c.), acidified with 4N-hydrochloric acid, and extracted continuously with ether for 16 hr. The ether extract afforded a solid (0·22 g.) which recrystallised from aqueous ethanol to give *pentafluorobenzenesulphanilide* (0·14 g.), m. p. 145° (Found: C, 44·7; H, 1·7; F, 29·0. $C_{12}H_6F_5NO_2S$ requires C, 44·5; H, 1·9; F, 29·4%).

The sulphonyl chloride (0·3 g.), phenol (0·1 g.), water (5 c.c.), and sodium hydroxide (0·1 g.) were shaken together at 16° for 4½ hr. and then poured into water. The solid (0·4 g.) obtained recrystallised from aqueous ethanol, to give *phenyl pentafluorobenzenesulphonate* (0·25 g.), m. p. 72·5° (Found: C, 44·2; H, 1·5; F, 29·9. $C_{12}H_5F_5O_3S$ requires C, 44·5; H, 1·5; F, 29·3%), $\lambda_{max.}$ 2740 Å (ε 1·69 × 10^3).

Ammination of Pentafluorobenzenesulphonyl Chloride.—The sulphonyl chloride (10 g.) was slowly added to an excess of ammonium carbonate (14·4 g.) and, after 17 hr. at 15° and ½ hr. at 100°, the mixture was added to water (100 c.c.). The precipitate (4·8 g.) was collected, washed with water, and recrystallised from water, to give *ammonium bis(pentafluorobenzenesulphon)imide* (4·0 g.), m. p. 303—305° (decomp.) (Found: C, 29·3; H, 1·0; F, 38·4. $C_{12}H_4F_{10}N_2O_4S_2$ requires C, 29·2; H, 0·8; F, 38·4%), $\nu_{max.}$ 3575, 3480, 3280, 3250, and 1425 (NH_4^+), 1500 (fluorinated benzene ring), and 1145 and 1330 cm.$^{-1}$ ($>SO_2$), $\lambda_{max.}$ 2200 (ε 1·1 × 10^4) and 2720 Å (ε 1·01 × 10^3).

The filtrate was acidified with 16N-hydrochloric acid, and the solid (0·4 g.) obtained was combined with that from the ether-extraction of the aqueous solution; recrystallisation from water gave *pentafluorobenzenesulphonamide* (1·6 g.), m. p. 156° (Found: C, 28·9; H, 0·9; F, 38·8. $C_6H_2F_5NO_2S$ requires C, 29·2; H, 0·8; F, 38·4%), $\nu_{max.}$ 3330 and 3240 (NH_2), 1505 (fluorinated benzene ring), 1364 and 1175 cm.$^{-1}$ ($>SO_2$), $\lambda_{max.}$ 2695 Å (ε 1·09 × 10^3).

Pentafluorobenzenesulphonyl chloride (1·75 g.) and aqueous ammonia (*d* 0·88; 20 c.c.) were shaken together for 2 hr. Addition of water (20 c.c.) gave ammonium bis(pentafluorobenzenesulphon)imide (0·4 g.), m. p. and mixed m. p. 283°. The filtrate was acidified and gave pentafluorobenzenesulphonamide (0·4 g.), m. p. and mixed m. p. 156°.

Bis(pentafluorobenzenesulphon)imide.—Ammonium bis(pentafluorobenzenesulphon)imide (0·12 g.), water (10 c.c.), and a cation-exchange resin (Amberlite, IR-A 120; 2 c.c.) were refluxed together for 15 min. and the resin was then removed and washed with hot water (10 c.c.). The combined filrate and washings were extracted with ether, and the ether solution was evaporated, leaving a solid which recrystallised from benzene to give *bis(pentafluorobenzenesulphon)imide* (0·05 g.), m. p. 163—164·5° (Found: C, 30·2; H, 0·5; S, 13·5. $C_{12}HF_{10}NO_4S_2$ requires C, 30·2; H, 0·2; S, 13·5%), $\nu_{max.}$ 3400 ($>NH$), 1630, 1525, 1490 (fluorinated benzene ring), and 1330, 1140 cm.$^{-1}$ ($>SO_2$), $\lambda_{max.}$ 2225 (ε 1·02 × 10^4) and 2715 Å (ε 1·73 × 10^3).

A Tetrafluoromethoxybenzenesulphonamide.—Pentafluorobenzenesulphonamide (0·4 g.) and sodium (0·04 g.) in dry (Mg) methanol (8 c.c.) were refluxed for 2¼ hr., then poured into water, acidified, and extracted with ether. Evaporation of the ether solution left a solid (0·32 g.) which recrystallised from water to give a *tetrafluoromethoxybenzenesulphonamide*, m. p. 125° (Found: C, 32·2; H, 1·8. $C_7H_5F_4NO_3S$ requires C, 32·4; H, 1·9%).

4-Aminotetrafluorobenzenesulphonamide.—Pentafluorobenzenesulphonamide (0·37 g.) was quickly added to a solution of sodium (1·5 g.) in liquid ammonia (60 c.c.) containing hydrated ferric nitrate (0·15 g.). After 1 hr. at −78°, ammonium chloride (10 g.) was added with vigorous stirring and the temperature was allowed to rise to 15°; during this process ether was added. The ether solution was filtered, dried ($MgSO_4$), filtered, and evaporated, leaving crystals (0·25 g.), m. p. 182—186°. Several recrystallisations from water gave 4-*aminotetrafluorobenzenesulphonamide* (0·10 g.), m. p. 202° (Found: C, 29·5; H, 1·6. $C_6H_4F_4N_2O_2S$ requires C, 29·5; H, 1·7%), with an i.r. spectrum identical with that of the compound obtained by an alternative method (see below) and $\lambda_{max.}$ 2560 Å (ε 4·58 × 10^3).

2,3,5,6-*Tetrafluorobenzenesulphonyl Chloride*.—Dry chlorine was briskly passed through a mixture of 2,3,5,6-tetrafluorothiophenol (19·5 g.), acetic acid (90 c.c.), and 80% w/v hydrogen peroxide (4 c.c.). After 2 hr. the mixture was poured into water and extracted with ether (3 × 150 c.c.), and the extracts were washed twice with saturated sodium metabisulphite solution, three times with saturated sodium hydrogen carbonate solution, and finally with water. The dried ($MgSO_4$) extracts were filtered and evaporated and the liquid residue was distilled, to give 2,3,5,6-*tetrafluorobenzenesulphonyl chloride* (15·6 g.), b. p. 224°/760 mm. [Found: C, 28·9 (water was added to facilitate combustion). $C_6HClF_4O_2S$ requires C, 29·0%.] $\nu_{max.}$ 3105 ($\geqslant$CH), 1515 (fluorinated benzene) and 1415 and 1195 cm.$^{-1}$ ($>SO_2$), $\lambda_{max.}$ 2835 Å (ε 3·02 × 10^3).

The sulphonyl chloride (0·3 g.), aniline (0·13 g.), water (10 c.c.), and sodium hydroxide (0·1 g.) were shaken together for 3 hr. at 15°, then poured into 4N-hydrochloric acid (10 c.c.). The precipitate (0·2 g.) was recrystallised from aqueous ethanol to give 2,3,5,6-*tetrafluorobenzenesulphanilide* (0·16 g.), m. p. 126·5—127° (Found: C, 47·1; H, 2·0; F, 24·6. $C_{12}H_7F_4NO_2S$ requires C, 47·2; H, 2·3; F, 24·9%).

The sulphonyl chloride (0·3 g.), phenol (0·12 g.), water (10 c.c.), and sodium hydroxide (0·13 g.) were shaken together at 16° for 3 hr. and afforded *phenyl* 2,3,5,6-*tetrafluorobenzenesulphonate* (0·16 g.), m. p. 88—89° (Found: C, 47·5; H, 1·8; F, 25·4. $C_{12}H_6F_4O_3S$ requires C, 47·1; H, 2·0; F, 24·8%).

The sulphonyl chloride (0·3 g.), pentafluorophenol (0·25 g.), water (10 c.c.), and sodium hydroxide (0·1 g.) similarly afforded *pentafluorophenyl* 2,3,5,6-*tetrafluorobenzenesulphonate* (0·17 g.), m. p. 91·5—92·5° (Found: C, 36·3; H, 0·2. $C_{12}HF_9O_3S$ requires C, 36·4; H, 0·25%), $\lambda_{max.}$ 2845 Å (ε 2·7 × 10^3).

Ammination of 2,3,5,6-*Tetrafluorobenzenesulphonyl Chloride*.—The sulphonyl chloride (2·1 g.) was slowly added to ammonium carbonate (2·9 g.). After 17 hr. at 15° and ½ hr. at 100°, water (20 c.c.) was added and the precipitate recrystallised from water, to give *ammonium bis*-(2,3,5,6-*tetrafluorobenzenesulphon*)*imide* (0·38 g.), m. p. 289—290° (Found: C, 31·1; H, 1·3; F, 32·9. $C_{12}H_6F_8N_2O_4S_2$ requires C, 31·4; H, 1·3; F, 33·2%), $\nu_{max.}$ 3500, 3400, 3190, 3210 (NH_4^+) 1490, 1600 (fluorinated benzene), and 1320 and 1175 cm.$^{-1}$ ($>SO_2$), $\lambda_{max.}$ 2200 Å (ε 9·79 × 10^3) and 2770 Å (ε 2·37 × 10^3).

The filtrate from the water-precipitation was acidified with 16N-hydrochloric acid, and the precipitate recrystallised from water to give 2,3,5,6-*tetrafluorobenzenesulphonamide* (0·86 g.), m. p. 145° (Found: C, 31·4; H, 1·2; F, 33·5. $C_6H_3F_4NO_2S$ requires C, 31·4; H, 1·3; F, 33·2%), $\nu_{max.}$ 3300 and 3200 (NH_2), 3020 ($\geqslant$CH), and 1503 cm.$^{-1}$ (fluorinated benzene), $\lambda_{max.}$ 2760 Å (ε 1·98 × 10^3).

Bis-(2,3,5,6-*tetrafluorobenzenesulphon*)*imide*.—The ammonium salt (0·21 g.), water (10 c.c.), and Amberlite IR-A 120 (2 c.c.) were refluxed for 15 min., filtered, and washed with water (10 c.c.). By ether-extraction of the combined filtrate and washings a solid was obtained which was recrystallised from water to give *bis*-(2,3,5,6-*tetrafluorobenzenesulphon*)*imide* (0·10 g.), m. p. 168—169° (Found: C, 32·4; H, 0·5; S, 14·7. $C_{12}H_3F_8NO_4S_2$ requires C, 32·6; H, 0·7; S, 14·5%), $\nu_{max.}$ 3400 ($>NH$) 3050 ($\geqslant$CH), 1600 and 1525 cm.$^{-1}$ (fluorinated benzene), $\lambda_{max.}$ 2215 (ε 1·26 × 10^4) and 2770 Å (ε 4·55 × 10^3).

2,3,5,6-*Tetrafluorobenzenesulphonic Acid*.—2,3,5,6-Tetrafluorobenzenesulphonyl chloride (1·2 g.), pyridine (20 c.c.), and water (5 c.c.) were kept at 20° for 18 hr. and then poured into 8N-hydrochloric acid. The solution was extracted continuously with ether for 24 hr. and the extracts were dried ($MgSO_4$), filtered, and evaporated, to leave a brown liquid (0·35 g.). Water (5 c.c.) was added and the solution divided into two parts. One part gave S-*benzylthiouronium*-2,3,5,6-*tetrafluorobenzenesulphonate* (0·04 g.), m. p. 161° (from water) (Found: C, 42·2; H, 3·2. $C_{14}H_{12}F_4N_2O_3S_2$ requires C, 42·4; H, 3·0%). The second portion with 50% w/v potassium hydroxide solution (10 c.c.) gave *potassium* 2,3,5,6-*tetrafluorobenzenesulphonate* (0·2 g.), m. p. >300° (from water), identical with the product of hydrolysis of 2,3,5,6-tetrafluorobenzenesulphonyl chloride by aqueous potassium hydroxide (Found: C, 26·6; H, 0·7; F, 27·9. $C_6HF_4KO_3S$ requires C, 26·5; H, 0·4; F, 28·3%).

Sulphonation of 1,2,4,5-*Tetrafluorobenzene.*—This compound (2·05 g.) and stabilised sulphur trioxide (9·0 g.) were kept at 15° for 19 hr., then poured on ice. Continuous ether-extraction for 16 hr. afforded the free sulphonic acid (1·50 g.) which was characterised as *S*-benzylthiouronium 2,3,5,6-tetrafluorobenzenesulphonate (0·25 g.), m. p. 164° alone and in admixture with that obtained in the above hydrolysis (Found: C, 42·5; H, 3·1%). The potassium salt was prepared also (Found: C, 26·7; H, 0·5; F, 28·1%) and its i.r. spectrum was identical with that of the potassium salt described above.

Sulphonation of 1,2,3,5-*Tetrafluorobenzene.*—This compound (1·2 g.) and stabilised sulphur trioxide (12·0 g.), treated as in the preceding case, gave S-*benzylthiouronium*-2,3,4,6-*tetrafluorobenzenesulphonate* (0·15 g. from 0·5 g. of acid), m. p. 153° (Found: C, 42·2; H, 2·9; F, 18·8. $C_{14}H_{12}F_4N_2O_3S_2$ requires C, 42·4; H, 3·0; F, 19·2%). The known [10] 1,2,3,4-tetrafluorobenzenesulphonic acid was prepared also by sulphonation of 1,2,3,4-tetrafluorobenzene; *S*-benzylthiouronium 1,2,3,4-tetrafluorobenzenesulphonate had m. p. 182° (lit.,[10] 182°) (Found: C, 42·6; H, 3·0; F, 19·7%).

4-*Acetamidotetrafluorothiophenol.*—Pentafluoroacetanilide (8·5 g.) in dimethylformamide (25 c.c.) was slowly added to a stirred suspension of sodium hydrogen sulphide (40 g.) in dimethylformamide (80 c.c.). After the initial reaction the mixture was kept at 110° for 5 min., then added to ice–water (250 c.c.) which was acidified with 8N-hydrochloric acid. The white precipitate (4·8 g.), m. p. 130—134°, was combined with the solid (3·65 g.; m. p. 130—134°) obtained by evaporation of the ether extracts of the filtrate. Recrystallisation from light petroleum (b. p. 80—100°) gave 4-*acetamidotetrafluorothiophenol*, m. p. 139° (Found: C, 39·8; H, 2·3. $C_8H_5F_4NOS$ requires C, 40·2; H, 2·1%), $\nu_{max.}$ 3200 ($>$NH), 2520 (SH), and 1520 cm.$^{-1}$ (fluorinated benzene), $\lambda_{max.}$ 2500 Å (ε 9·3 × 10^3).

The thiol (0·3 g.) and chloro-2,4-dinitrobenzene (0·5 g.) in ethanol (15 c.c.) were refluxed for 1 hr., then poured into water, and the precipitate was recrystallised from ethanol, to give pale yellow needles of 4-*acetamidotetrafluoro*-2′,4′-*dinitrodiphenyl sulphide* (0·4 g.), m. p. 250—252° (decomp.) (Found: C, 41·6; H, 1·7. $C_{14}H_7F_4N_3O_5S$ requires C, 41·5; H, 1·7%).

Desulphurisation of 4-*Acetamidotetrafluorothiophenol.*—This compound (2·1 g.) and Raney nickel (grade W4; 25 g.) in methanol (150 c.c.), in the usual way, gave a solid (1·4 g.) which was purified by chromatography on alumina and then recrystallisation from aqueous ethanol, to give 2,3,5,6-tetrafluoroacetanilide (0·9 g.), m. p. 137—138° alone and in admixture with an authentic specimen; [1,6] it displayed a correct i.r. spectrum.

Di-(4-*acetamidotetrafluorophenyl*) *Disulphide.*—Bromine (0·13 c.c.) was slowly added to a stirred solution of 4-acetamidotetrafluorothiophenol (0·98 g.) in glacial acetic acid (15 c.c.) at 30° until the bromine colour just persisted. After 1 hr. at 15° the solvent was removed *in vacuo*, to leave a white solid (0·85 g.) which recrystallised from acetic acid, to give *di*-(4-*acetamidotetrafluorophenyl*) *disulphide* (0·6 g.), m. p. 268—270° (decomp.) (Found: C, 40·5; H, 1·7; S, 13·1. $C_{16}H_8F_8N_2O_2S_2$ requires C, 40·3; H, 1·7; S, 13·5%), $\lambda_{max.}$ 2500 (ε 1·96 × 10^4) and 2570 Å (ε 1·96 × 10^4).

4-*Aminotetrafluorothiophenol.*—4-Acetamidotetrafluorothiophenol (2·0 g.) and 11N-sulphuric acid (25 c.c.) were kept at 105° for 45 min., then poured into water, and the solution was extracted with ether (3 × 100 c.c.). The ether extracts afforded a yellow solid (1·2 g.) which was recrystallised from benzene–light petroleum (b. p. 80—100°), to give 4-*aminotetrafluorothiophenol* (0·8 g.), m. p. 145—148° (Found: C, 36·6; H, 1·7. $C_6H_3F_4NS$ requires C, 36·5; H, 1·5%), $\nu_{max.}$ 3500, 3400 (NH_2), 2600 (SH), 1630 and 1510 cm.$^{-1}$ (fluorinated benzene ring).

Oxidation of 4-*Acetamidotetrafluorothiophenol with Chlorine, Water, and Acetic Acid.*—Dry chlorine was briskly bubbled through a solution of the thiol (3·0 g.) in glacial acetic acid (33 c.c.) containing water (0·58 c.c.) for 2½ hr. The intermediate disulphide was precipitated very quickly, but slowly dissolved. The mixture was added to water (150 c.c.) and extracted with ether (3 × 100 c.c.). The extract was washed successively with saturated aqueous sodium metabisulphite (twice), aqueous sodium hydrogen carbonate (thrice), and water, dried ($MgSO_4$), filtered, and evaporated. The residual white solid (1·9 g.), which became discoloured when kept at 100°, crystallised from chloroform to give colourless needles of 4-*acetamidotetrafluorobenzenesulphonyl chloride* (1·2 g.), m. p. 163·5—165° (Found: C, 31·5; H, 1·4; S, 10·7. $C_8H_4ClF_4NO_3S$ requires C, 31·4; H, 1·3; S, 10·5%), $\nu_{max.}$ 3190 ($>$NH), 1515 (fluorinated benzene), 1392 and 1182 cm.$^{-1}$ ($>SO_2$), $\lambda_{max.}$ 2640 Å (ε 4·73 × 10^3).

The aqueous phase was acidified with 16N-hydrochloric acid and continuously extracted with ether for 18 hr. The dried ($MgSO_4$) extracts were filtered and evaporated. Acetic acid was removed *in vacuo*, to leave a solid (0·6 g.) which recrystallised from benzene to give 2,3,5,6-tetrafluoroacetanilide (0·4 g.), m. p. 140—140·5° alone and in admixture with an authentic specimen[1,6] (Found: C, 46·3; H, 2·4. Calc. for $C_8H_5F_4NO$: C, 46·3; H, 2·4%) (correct i.r. spectrum).

Oxidation of 4-*Acetamido*-2,3,5,6-*tetrafluorothiophenol with Chlorine, Water, Hydrogen Peroxide, and Acetic Acid.*—Dry chlorine was briskly bubbled through a solution of the thiol (2·3 g.) in glacial acetic acid (30 c.c.) containing 80% w/v aqueous hydrogen peroxide (0·35 c.c.) for 3 hr. The disulphide was soon precipitated but slowly dissolved. The previously described procedure afforded 4-acetamidotetrafluorobenzenesulphonyl chloride (0·3 g.), m. p. 163—165°, and 2,3,5,6-tetrafluoroacetanilide (0·8 g.), m. p. 140°.

In some of a series of reactions a small amount of crystals was obtained which recrystallised from benzene–light petroleum (b. p. 80—100°), to give a *chlorotetrafluoroacetanilide*, m. p. 142—143° (Found: C, 39·6; H, 1·6. $C_8H_4ClF_4NO$ requires C, 39·8; H, 1·7%), $\nu_{max.}$ 3196 ($>$NH) and 1530 cm.$^{-1}$ (fluorinated benzene ring).

4-*Aminotetrafluorobenzenesulphonamide.*—4-Acetamidotetrafluorobenzenesulphonyl chloride (0·28 g.) and aqueous ammonia (*d* 0·88; 5 c.c.) were shaken together at 16° for 2 hr. and an equal volume of water was added. The solution was acidified with 16N-hydrochloric acid and extracted with ether. The dried ($MgSO_4$) extract was filtered and evaporated, to leave 4-acetamidotetrafluorobenzenesulphonamide (0·19 g.), m. p. 180—182°, which was not purified but was refluxed with 16N-hydrochloric acid (2 c.c.) and water (10 c.c.) for 1 hr. When this solution was cooled, neutralised with sodium hydrogen carbonate, and extracted with ether (3 × 20 c.c.) and the extract dried ($MgSO_4$) and evaporated, a solid (0·14 g.) was obtained which recrystallised from water to give 4-aminotetrafluorobenzenesulphonamide, m. p. 203·5—205° alone and in admixture with material prepared by an alternative synthesis. The i.r. spectrum was identical with that of the compound obtained from sodamide and pentafluorobenzenesulphonamide in liquid ammonia (see above); $\nu_{max.}$ were at 3500, 3380, and 3275 (NH_2), 1505 (fluorinated benzene), 1350 and 1169 cm.$^{-1}$ ($>SO_2$).

4-*Aminotetrafluorobenzenesulphanilide.*—(*a*) The sulphonyl chloride (0·28 g.), aniline (0·11 g.), sodium hydroxide (0·1 g.), and water (10 c.c.) were shaken together for 2 hr. at 16° and poured into water (30 c.c.). The very dark mixture was extracted with ether (3 × 30 c.c.), and the extracts were dried ($MgSO_4$), filtered, and evaporated to leave aniline (0·08 g.) (correct infrared spectrum). The aqueous phase from the extraction was acidified with 16N-hydrochloric acid and extracted continuously with ether; the extract afforded an intractable tar (0·04 g.). (*b*) The sulphonyl chloride (0·28 g.) and aniline were shaken together for 1 hr. at 16°. Dry benzene (5 c.c.) was then added and, after 30 minutes' refluxing, the solvent was evaporated, to leave 4-acetamidotetrafluorobenzenesulphanilide (0·25 g.), m. p. 182°, which was not purified further but was refluxed with 4N-hydrochloric acid (10 c.c.) and ethanol (5 c.c.) for 1½ hr. The organic solvents were evaporated, an excess of sodium hydrogen carbonate was added, and the mixture was extracted with ether, to afford a solid (0·21 g.) which was recrystallised from aqueous ethanol to give 4-*aminotetrafluorobenzenesulphanilide*, m. p. 284·5—285·5° (Found: C, 45·0; H, 2·9; S, 10·1. $C_{12}H_8F_4N_2O_2S$ requires C, 45·0; H, 2·5; S, 10·0%), $\nu_{max.}$ 3450, 3375, and 3275 ($>$NH and NH_2), 1521 (fluorinated benzene), 1347 and 1168 cm.$^{-1}$ ($>SO_2$), $\lambda_{max.}$ 2670 Å (ε 2·37 × 10^4).

We thank Professor M. Stacey, F.R.S., for his interest, Dr. L. F. Thomas for the magnetic measurements, the University for a scholarship (to P. R.), and the D.S.I.R. for a maintenance award (to T. A. S.).

CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

[*Received, January 8th*, 1963.]