Synthesis and reactions of 4-sulpho-2,3,5,6,-tetrafluorobenzoic acid

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Abstract

4-Sulpho-2,3,5,6-tetrafluorobenzoic acid (**I**) has been synthesised from pentafluorobenzoic acid via the oxidation of 4-mercapto-tetrafluorobenzoic acid. Reaction of **I** with DMF/$SOCl_2$ gave 1,4-ClC_6F_4COCl (**IIA**) which was converted to 1,4-ClC_6F_4COF (**IIB**) by fluoride exchange. Reaction with methanol or aniline gave respectively the methyl ester 1,4-$ClC_6F_4CO_2Me$ (**IIIA**) and anilide 1,4-$ClC_6F_4CONHPh$ (**IIIB**). Treatment of **I** with PCl_5 gave the diacid chloride 1,4-$ClOCC_6F_4SO_2Cl$ (**IVA**) which was converted to **IIB** by the action of KF in tetraglyme. Stoichiometric reaction of **I** with SF_4 gave 1,4-$FOCC_6F_4SO_2F$ (**IVB**) while the use of excess reagent produced 1,4-$F_3CC_6F_4SO_2F$ (**V**). Partial hydrolysis of **IVB** gave 1,4-$HO_2CC_6F_4SO_2F$ (**VIA**) which was decarboxylated in DMSO to give 1,4-$HC_6F_4SO_2F$ (**VII**). The diacid halides **IVA** and **IVB** were readily derivatised with methanol or aniline to give respectively 1,4-$MeO_2CC_6F_4SO_2Cl$ (**VIIIA**), 1,4-$MeO_2CC_6F_4SO_2F$ (**VIB**), 1,4-$PhNHOCC_6F_4SO_2Cl$ (**VIIIB**) and 1,4-$PhNHOCC_6F_4SO_2F$ (**VIC**). Treatment of **IVB** with ethylene glycol gave 1,4-$[CH_2O_2CC_6F_4SO_2F]_2$ (**IX**). Reaction of the methyl esters **VIB** and **VIIIA** with equimolar amounts of aniline afforded respectively (3-PhNH)-1,4-$MeO_2CC_6F_3SO_2F$ (**X**) and 1,4-$MeO_2CC_6F_3SO_2NHPh$ (**XI**). Analogous reaction of aniline with $C_6F_5SO_2F$ gave 1,4-$PhHNC_6F_4SO_2F$.

Introduction

The three isomers of the hydrocarbon sulphobenzoic acids are well-known compounds [1] and are usually prepared by the oxidation of the appropriate toluenesulphonic acid, mercaptobenzoic acid or di(carboxyphenyl)disulphide. The compounds have been used for a number of applications. For example, all three isomers or their derivatives have been claimed and/or used in polymer systems as additives [2], initiators [3], catalysts or as construction units [4]. A range of derivatives have also been made and tested for their biological activity [5]. In particular, the sulphinimide derivative of the *ortho* isomer, saccharin, is an important commercial product.

Although the isomers of tetrafluorobenzene dicarboxylic acids are well known and the isomers of tetrafluorobenzene disulphonic acid have recently been reported by Satori and coworkers [6], comparatively few reports [7–14] document tetrahaloaromatic analogues or derivatives of the sulphobenzoic acids. Where these occur the compounds described are usually the tetra-

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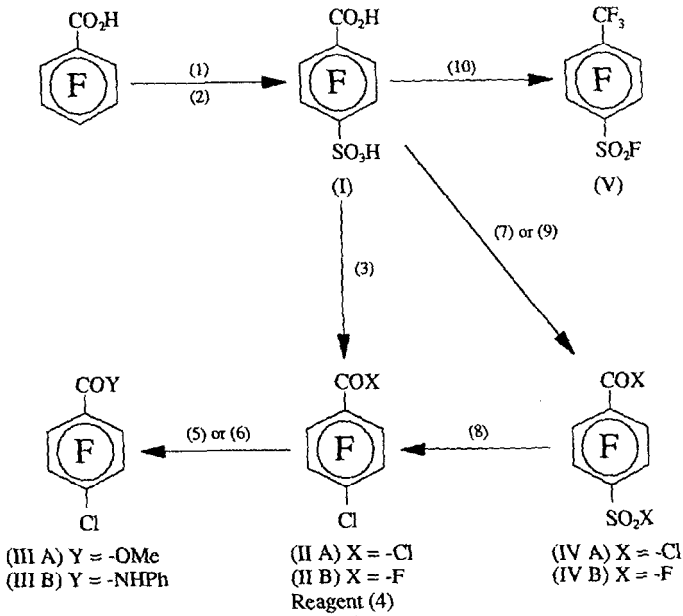
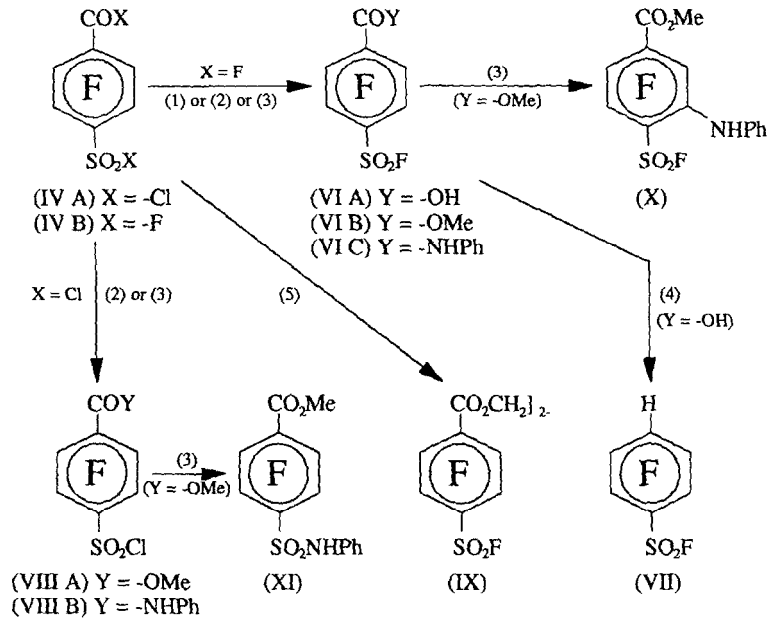


Scheme 1. Synthesis and some reactions of 4-sulphotetrafluorobenzoic acid. (1) NaSH, NaOH, H_2O; (2) H_2O_2, AcOH; (3) DMF, $SOCl_2$; (4) NaF, tetraglyme, Ph_4PBr; (5) MeOH; (6) $PhNH_2$; (7) PCl_5, $POCl_3$; (8) KF, CaF_2, tetraglyme; (9) SF_4; (10) excess SF_4.



Scheme 2. Reactions of 4-sulphotetrafluorobenzoic acid dihalides. (1) H_2O; (2) MeOH; (3) $PhNH_2$; (4) DMSO, heat; (5) $HOCH_2CH_2OH$.

bromo, -chloro and -iodo derivatives of only the *ortho*-sulphobenzoic acid isomer.

We have investigated the synthesis and some reactions of 1,2- and 1,4-tetrafluorosulphobenzoic acids and report here on the *para* isomer. Reactions are illustrated in Schemes 1 and 2.

Experimental

General methods

GLC analysis

Analyses were done using a Perkin-Elmer 8500 gas chromatograph fitted with a 25 m BP1 capillary column operating under either of the following programmes: (1) 100 °C for 1 min, 20 °C min^{-1} to 200 °C, 200 °C isothermal for 15 min; (2) 50–200 °C at 20 °C min^{-1}, 200 °C isothermal for an appropriate time.

HPLC analysis

Analyses were done using a Spherisorb 5 μm silica column fitted with 2-cm precolumn in a Perkin-Elmer series 3B liquid chromatograph coupled to a refractive index detector operating at 35 °C.

Mass spectra

Obtained using a VG 70-70E mass spectrometer, either by the direct insertion technique or by combined gas–liquid chromatography (25-m BP1, 0.25 μm column).

Infrared spectra

Solid- and liquid-phase spectra were recorded respectively as KBr discs or as thin films using a Perkin-Elmer 882 spectrophotometer (slit 1, filter 0.25, smooth 1, resolution 5.4 cm^{-1}). Gas-phase spectra were obtained using a 25-m BP1 capillary column (programme 2) in a Perkin-Elmer 8310 gas chromatograph coupled to a Nicolet 20SX spectrophotometer.

Melting points

Measured on the hot stage of a Reichert Thermovar microscope and are reported uncorrected.

NMR spectra

^{19}F spectra, referenced against CCl_3F, were obtained using a Jeol FX-100 spectrometer operating at 93.65 MHz. ^{13}C and ^{1}H spectra were recorded using a Brucker AM-500 spectrometer operating at 125 and 500 MHz, respectively.

CFC113 [1,2,2-trichloro-1,1,2-trifluoroethane, $CF_2Cl-CCl_2F$] was used extensively as a solvent.

4-Mercapto-2,3,5,6-tetrafluorobenzoic acid

A solution of pentafluorobenzoic acid (850 g, 4.03 mol) in aqueous sodium hydroxide (160 g, 4.0 mol in 2.25 l water) was added slowly to a

stirred solution of sodium hydrosulphide (400 g, 5.0 mol) in aqueous sodium hydroxide (160 g, 4.0 mol in 750 ml water). The mixture was stirred at 70 °C for 2 h, cooled and acidified (conc. HCl). Released H_2S was trapped in a sodium hypochlorite scrubbing tower. The white precipitate was extracted into ether and the solvent was evaporated under reduced pressure, affording crude product (827 g) which could be recrystallised from petroleum ether to give the title compound, m.p., 149–151 °C (lit. value [18], 148–150 °C; lit. value [17], 156–158 °C). For NMR data see Table 1. MS *m/z*: 226 (100%, M^+); 289 (64); 197 (7); 181 (12); 162 (10); 150 (13); 137 (30); 117 (17); 111 (14); 99 (10); 93 (10); 87 (16); 79 (6); 69 (7); 63 (12). IR (KBr) $\tilde{\nu}$: 3083 (s); 2592 (w); 1702 (s); 1638 (s); 1476 (s); 1416 (m); 1387 (w); 1307 (m); 1232 (m); 1022 (s); 916 (m); 857 (w); 722 (m) cm^{-1}.

4-Sulpho-2,3,5,6-tetrafluorobenzoic acid (I)

Hydrogen peroxide (30%, 1.6 l, 14 mol) was added to a stirred solution of 4-mercaptotetrafluorobenzoic acid (894 g, 4.2 mol) in acetic acid (4 l) at such a rate that the temperature was maintained between 65–70 °C. When all the oxidant had been added, the mixture was heated for a further 2 h at 70 °C and then cooled to room temperature. Excess peroxide was destroyed by the addition of $Na_2S_2O_5$ and most of the liquid phase was removed under reduced pressure. The resulting slurry was extracted with ethyl acetate from which a water-soluble fraction was then back-extracted into water. The water was removed under reduced pressure and the solid residue was dried to constant weight at 60 °C/0.5 mbar pressure to give the title compound (978 g). For NMR data see Table 1. MS *m/z* (direct insertion, probe at 200 °C): 274 (100%, M^+); 257 (20); 230 (30); 193 (26); 166 (17); 149 (38); 137 (25); 118 (23); 99 (53); 79 (17). IR (KBr) $\tilde{\nu}$: 3500–2400 (br, −COOH); 3410 (s); 3045 (s); 1708 (s, −COOH); 1631 (m); 1467 (s); 1412 (s); 1295 (s); 1229 (s); 1156 (w); 1066 (s); 980 (s); 906 (w); 831 (w); 720 (m); 653 (m); 609 (w) cm^{-1}. Drying temperatures of 60–80 °C were employed as at temperatures above 100 °C the material discoloured. However, no chemical change was detected by NMR or IR spectroscopy when the diacid was heated at 150 °C for 4 h under nitrogen.

4-Chloro-2,3,5,6-tetrafluorobenzoyl chloride (IIA)

A mixture of crude (not purified by back-extraction into water) 4-sulphotetrafluorobenzoic acid (**I**) (6.7 g, 24.5 mmol), dimethyl formamide (0.5 g, 6.9 mmol) and thionyl chloride (24.6 g, 206.7 mmol) was gently refluxed for 6 h. The product was filtered and excess reagent was removed from the filtrate under reduced pressure to leave a yellow oil (7.9 g). Distillation gave an enriched fraction (5.0 g) boiling below 100 °C at 0.3 mbar pressure. GLC analysis (programme 1) showed one major (75%, 2.0 min) and several minor (11%, 1.1 min; 4%, 1.2 min; 4%, 2.4 min; 2%, 4.0 min) products. The major peak eluted after 3.4 min using programme 2. Spectral analysis of the mixture indicated that the major product was 4-chloro-2,3,5,6-tetrafluorobenzoyl chloride. For NMR data see Table 1.

TABLE 1

NMR data for compounds 1,4-X−C_6F_4−Y

Structure (Schemes 1 & 2)	Substituent X	Substituent Y	Solvent	Nucleus	C_6F_4 [a] 1 (*J* Hz)	4 (*J*, Hz)	2/6 (*J*, Hz)	3/5 (*J*, Hz)	X(1) COX′	Y(4) SO_2F	Other
–	CO_2H	SH	CD_3OD	F	–	–	[−137.9 and −140.4]		–	–	–
				C	118.5 (21.5)	111.6	[145.2 and 146.5] (244.1 and 254.9)		162.5	–	–
I	CO_2H	SO_3H	DMSO-d_6	F	–	–	−140.5	−138.1	–	–	–
				C	128.7	114.6	[143.0 and 145.2]		161.2	–	–
IIA	COCl	Cl	$CDCl_3$	F	–	–	−138.3 [108.3 and 111.0]	−138.3	–	–	–
				C			[137.3 and 137.3] (251)	(251)	150.9	–	–
IIB	COF	Cl	$CDCl_3$	F	–	–	−134.5	−138.5	47.1 (40.2)	–	–
				C	105.4 (66.3d, 12.6, t)	120.7 (18t)	146.2 (262)	146.2 (262)	149.1 (344.7)	–	–
IIIA	CO_2Me	Cl	$CDCl_3$	F	–	–	−138.8	−139.9	–	–	–
				C	111.4 (16.2)	115.6 (18.0)	[144.8 and 144.1] (251, 258.5)		159.2	–	52.9 (OCH_3)
				H	–	–	–	–	–	–	(3.9 (s, OCH_3)
IVA	COCl	SO_2Cl	neat	F	–	–	−135.2	−133.0	–	–	–
				C	126.1 (12.6)	122.6 (16.2)	144.0 (270)	144.0 (270)	158.0	–	–
IVB	COF	SO_2F	$CDCl_3$ CFC113	F	–	–	−131.4	−131.4	−50.0	73.2	–
				C	119.5 (69.6, d; 12.2, t)	113.5 (34.8, d 12.2, t)	[144.9 and 146.8] (247, d; 247, d)		147.4 (348, d)	–	–

(*continued*)

TABLE 1 (*continued*)

Structure (Schemes 1 & 2)	Substituent X	Substituent Y	Solvent	Nucleus	C_6F_4 [a] 1 (J Hz)	4 (J, Hz)	2/6 (J, Hz)	3/5 (J, Hz)	X(1) COX′	Y(4) SO_2F	Other
V	CF_3	SO_2F	$CDCl_3$	F	–	–	−134.8	−131.1	–	73.0	−57.5 (CF_3)
				C	116.7 (36.0, q 12.4, t)	117.9 (36.2, d; 14.3, t)	[144.9 and 144.6] (*c.* 260)	(*c.* 260)	–	–	120.0 (CF_3) (277)
VIA	CO_2H	SO_2F	CD_3OD	F	–	–	−137.1	−134.1	–	73.2 (14.6)	–
				C	122.8 (18)	116.6 (32, d; (18, t)	146.3 (267)	146.3 (267)	160.6	–	–
VIB	CO_2Me	SO_2F	$CDCl_3$	F	–	–	−135.0	−132.5	–	73.1	–
				C	119.9 (17.1)	116.3 (30.5, 13)	[144.9 and 144.4]		158.2	–	54.1 (OCH_3)
				H	–	–	–	–	–	–	4.03 (OCH_3)
VII	H	SO_2F	$CDCl_3$	F	–	–	−134.1	−134.1	–	72.6	–
				C	113.4	114.9	[146.5 and 144.2] (*c.* 270)	(*c.* 270)	–	–	–
				H	7.5 (8)	–	–	–	–	–	–
VIIIA	CO_2Me	SO_2Cl	$CDCl_3$	F	–	–	−135.2	−133.9	–	–	–
				C	125.0 (12.6)	119.3 (18.0)	[143.6 and 144.6] (262 and 269)		158.1	–	54.0 (OCH_3)
				H	–	–	–	–	–	–	4.1 (OCH_3)
IX	$[CO_2CH_2]_2$	SO_2F	DMSO-d_6	F	–	–	−136.2	−133.8	–		–
				C	117.9 (16.2, t)	115.0 (32.3, d; 12.6, t)	[144.1 and 144.1]		157.2	–	64.4 ($-CH_2-$)
				H	–	–	–	–	–	–	4.81 ($-CH_2-$)

[a]Square brackets [ ] denote uncertain assignment between signals bracketed.

Combined GLC–MS and GLC–IR analysis of the major product gave *m/z* 246 (12%, M^+); 211 (100); 183 (43); 176 (5); 148 (11); 133 (32); 117 (12); 106 (7); 98 (21); 93 (5); 79 (17), and $\tilde{\nu}$ (gas phase) 1852 (s); 1635 (w); 1495 (s); 1414 (w); 1310 (s); 1141 (s); 997 (m); 965 (w); 854 (m); 690 (m) cm^{-1}.

4-Chloro-2,3,5,6-tetrafluorobenzoyl fluoride ***(IIB)***

A mixture of the above enriched 4-chloro-2,3,5,6-tetrafluorobenzoyl chloride (**IIA**) (3.15 g), dry sodium fluoride (1.0 g), tetraphenylphosphonium bromide (0.06 g) and tetraglyme (7.5 g) was heated for 10 h at 155 °C under dry nitrogen. Material boiling below 80 °C at 3 mbar was removed by distillation. Spectral analysis indicated that the major product eluting at 2.5 min on GLC analysis (programme 2) was 4-chloro-2,3,5,6-tetrafluorobenzoyl fluoride. For NMR data see Table 1. Combined GLC–MS and GLC–IR analysis gave *m/z* 232 (33); 231 (7); 230 (100%, M^+); 213 (12); 211 (36); 204 (22); 202 (67); 195 (10); 185 (8); 183 (26); 180 (7); 167 (19); 148 (8); 135 (10); 133 (27); 117 (32); 109 (5); 98 (14); 93 (6); 79 (10), and $\tilde{\nu}$ (gas phase) 1796 (s); 1636 (w); 1492 (s); 1412 (w); 1292 (m); 1056 (m); 990 (s); 890 (w); 777 (s); 720 (s) cm^{-1}.

Methyl 4-chloro-2,3,5,6-tetrafluorobenzoate ***(IIIA)***

Dry methanol was added slowly to 4-chloro-2,3,5,6-tetrafluorobenzoyl fluoride (**IIB**) (2.5 g, 10.9 mmol) in dry ether (25 ml). The mixture was washed with water, partitioned and the solvent evaporated leaving a colourless liquid. Distillation gave the title compound (1.1 g), b.p., 93–96 °C/0.3 mbar, which on GLC (programme 2) eluted at 4.2 min. For NMR data see Table 1. Combined GLC–MS and GLC–IR spectral analysis of the 4.2 min peak gave *m/z* 244 (8); 243 (3); 242 (M^+, 25%); 213 (33); 212 (8); 211 (100); 185 (9); 184 (3); 183 (25); 148 (8); 135 (6); 133 (18); 117 (7); 109 (4); 98 (12); 79 (8); 59 (9), and $\tilde{\nu}$ (gas phase) 1766 (s); 1491 (s); 1440 (w); 1312 (s); 1213 (s); 991 (m); 755 (m) cm^{-1}. The liquid-phase infrared spectrum was similar except for the >CO band which appeared at 1746 cm^{-1}.

4-Chloro-2,3,5,6-tetrafluoro-N-*benzanilide* ***(IIIB)***

A solution of aniline (0.75 g, 8.1 mmol) in dichloromethane (3 ml) was added dropwise to a stirred ice-chilled solution of 4-chloro-2,3,5,6-tetrafluorobenzoyl fluoride (**IIB**) (*c.* 0.75 g, 3.25 mmol) in dichloromethane (5 ml). The mixture was left at room temperature for 1 h when volatiles were removed under reduced pressure, water was added to the residue and the mixture was extracted with ether. Evaporation of the ether gave a gum (1.5 g) which was purified by column chromatography (35 g silica, 20% ethyl acetate in hexane as eluent) affording a solid which was recrystallised from hexane to give as long needles the title compound (0.32 g), m.p., 180 °C (sub.). For NMR data see Table 2. Combined GLC–MS (of direct insertion technique, probe at 200 °C) gave *m/z*: 305 (13); 304 (7); 303 (40, M^+);

213 (32); 212 (12); 211 (100); 185 (7); 184 (3); 183 (17); 148 (5); 133 (8); 94 (11); 65 (15); 51 (5). IR (KBr) $\tilde{\nu}$: 3242 (w); 3080 (w); 1685 (m); 1656 (s); 1606 (m); 1566 (m); 1495 (m); 1482 (s); 1446 (m); 1404 (w); 1338 (m); 978 (s); 892 (w); 852 (w); 774 (w); 746 (m); 690 (w) cm^{-1}. GLC analysis (programme 2) showed a single broad peak eluting at 11.1 min.

4-Chlorosulphonyl-2,3,5,6-tetrafluorobenzoyl chloride (IVA)

A stirred mixture of dry 4-sulpho-2,3,5,6-tetrafluorobenzoic acid (**I**) (10 g, 36.5 mmol), phosphorus pentachloride (18.5 g, 88.9 mmol) and phosphoryl chloride (5 ml) was heated at 60 °C under nitrogen for 2 h, when undissolved solid was removed by filtration. The filtrate was fractionally distilled to give the title compound (8.0 g), b.p., 101–102 °C/0.2 mbar. For NMR data see Table 1. MS *m/z*: 312 (5%); 310 (7, M^+); 277 (37); 276 (10); 275 (100); 213 (8); 212 (8); 211 (22); 192 (11); 183 (12); 177 (48); 176 (62); 149 (30); 148 (49); 136 (6); 133 (10); 117 (22); 99 (25); 98 (35); 93 (6); 79 (18); 74 (7); 64 (34); 48 (23). IR (film) $\tilde{\nu}$: 1794 (sh); 1768 (s); 1494 (s); 1406 (s); 1296 (s); 1254 (m); 1186 (s); 1064 (s); 996 (s); 862 (s); 794 (m); 768 (m); 728 (s) cm^{-1}. GLC analysis (programme 2) showed a single peak eluting at 6.1 min.

Reactions with sulphur tetrafluoride

All reactions were undertaken in Hastelloy C autoclaves. The autoclave was charged with 4-sulphotetrafluorobenzoic acid (**I**) and an approximately 3.5 molar excess of thionyl chloride, sealed and left at ambient temperature for 18 h. Unreacted $SOCl_2$, SO_2 and HCl were removed by heating to 80 °C while progressively reducing the pressure. The vessel was then evacuated, cooled in liquid nitrogen and the calculated quantity of SF_4 introduced. The reaction mixture was heated to 80 °C and stirred at this temperature for 18 h. The vessel was then cooled to room temperature, vented and the residual volatile material removed under reduced pressure. CFC113 was added and the soluble reaction products were removed. Evaporation of the solvent gave the crude reaction product which was purified by distillation or recrystallisation.

4-Fluorosulphonyl-2,3,5,6-tetrafluorobenzoyl fluoride (IVB)

Prepared as above from 4-sulphotetrafluorobenzoic acid (**I**) (150 g, 0.55 mol) and sulphur tetrafluoride (96 g, 0.89 mol). Workup gave the moisture-sensitive title compound (71% yield based on SF_4), b.p., 62–64 °C/0.4 mbar, m.p., 44–46 °C (recrystallised from iso-octane), eluting at 3.2 min on GLC analysis (programme 2). The diacid fluoride was hydrolytically stable for at least 3 weeks when stored under dry nitrogen either as the free compound or as a CFC113 solution. For NMR data see Table 1. MS *m/z*: 278 (M^+, 100%); 259 (12); 250 (5); 228 (9); 207 (5); 195 (21); 186 (20); 184 (20); 167 (35); 155 (26); 148 (14); 117 (92); 98 (21); 93 (15); 67 (23). IR (film) $\tilde{\nu}$: 1834 (s, −COF); 1515 (sh); 1495 (s); 1438 (m); 1316 (s); 1260 (s); 1230 (s); 1146 (s); 1006 (s); 964 (s); 844 (m); 798 (s); 692 (m) cm^{-1}.

4-Trifluoromethyl-2,3,5,6-tetrafluorobenzenesulphonyl fluoride (V)

Prepared as above from 4-sulphotetrafluorobenzoic acid (**I**) (25 g, 91 mmol) and sulphur tetrafluoride (32 g, 296 mmol). Workup gave the title compound (24 g, 95%), b.p., 54–55 °c/0.3 mbar, m.p., 35–38 °C (recrystallised from iso-octane), eluting at 2.3 min on GLC analysis (programme 2). For NMR data see Table 1. Combined GLC–MS and GLC–IR gave *m/z* 300 (100%, M^+); 281 (27); 236 (15); 217 (68); 205 (32); 198 (9); 186 (18); 179 (8); 167 (22); 155 (18); 148 (2); 129 (7); 117 (28); 98 (12); 93 (14); 79 (8); 69 (23); 67 (28), and $\bar{\nu}$ 1504 (s); 1458 (w); 1333 (s); 1242 (w); 1181 (s); 998 (m); 952 (m); 834 (w); 805 (m); 718 (w) cm^{-1}.

4-Fluorosulphonyl-2,3,5,6-tetrafluorobenzoic acid (VIA)

Water (1.0 ml, 55.6 mmol) was added to a solution of 4-fluorosulphonyl-2,3,5,6-tetrafluorobenzoyl fluoride (**IVB**) (*c.* 12 g, 43.5 mmol) in CFC113 (30 ml) and the mixture was stirred at room temperature for 24 h. Volatiles were removed under reduced pressure, the residue was taken up in ether and washed with water. Evaporation of the ether afforded crude product (11.3 g) which was purified either by sublimation (140 °C/0.3 mbar, 80% recovery) or by recrystallisation from 1% ethyl acetate in hexane, to give the title compound, m.p., 133–135 °C. For NMR data see Table 1. MS *m/z* (direct insertion, probe at 200 °C): 276 (100%, M^+); 259 (40); 232 (83); 212 (7); 193 (5); 192 (12); 176 (14); 168 (40); 149 (66); 148 (23); 137 (60); 129 (12); 117 (27); 99 (80); 98 (24); 93 (12); 86 (5); 80 (10); 79 (17); 75 (13); 74 (5); 69 (8); 67 (16); 64 (6); 48 (7); 45 (25); 44 (43). IR (KBr) $\bar{\nu}$: 3016 (br, s); 1736 (s); 1690 (w); 1648 (w); 1608 (w); 1510 (s); 1492 (s); 1475 (sh); 1444 (m); 1420 (m); 1294 (s); 1250 (m); 1212 (s); 995 (s); 842 (m); 793 (m); 713 (m) cm^{-1}.

Methyl 4-fluorosulphonyl-2,3,5,6-tetrafluorobenzoate (VIB)

Dry methanol (4 ml) was added to a solution of 4-fluorosulphonyl-2,3,5,6-tetrafluorobenzoyl fluoride (**IVB**) (*c.* 5.6 g, 20 mmol) in CFC113 (10 ml) and the mixture was stirred under dry nitrogen for 18 h. Volatiles were removed under reduced pressure and the solid residue (6.14 g) was purified by column chromatography (45 g silica 20% ethyl acetate in hexane as eluent) affording a low-melting solid (5.38 g, 94%) which was recrystallised from 1% ethyl acetate in hexane to give the title compound (3.75 g), m.p., 46 °C. GLC analysis (programme 2) showed a single peak eluting at 5.3 min. For NMR data see Table 1. MS *m/z*: 290 (33%, M^+); 271 (5); 259 (100, P^+); 207 (4); 192 (22); 176 (24); 164 (5); 148 (25); 136 (8); 129 (4); 117 (17); 98 (20); 79 (10); 67 (5); 59 (25). IR (KBr) $\bar{\nu}$: 2970 (w); 1744 (s); 1508 (s); 1490 (s); 1434 (s); 1324 (s); 1264 (m); 1245 (m); 1212 (s); 1185 (w); 1020 (m); 996 (s); 924 (w); 854 (m); 794 (m); 756 (m); 696 (w); 618 (s) cm^{-1}. Ethyl 4-fluorosulphonyl-2,3,5,6-tetrafluorobenzoate was similarly prepared and eluted at 5.9 min on GLC analysis (programme 2).

4-Fluorosulphonyl-2,3,5,6-tetrafluorobenzanilide (VIC)

Aniline (3.4 g, 36.6 mmol) was added dropwise under nitrogen to a stirred ice-chilled solution of 4-fluorosulphonyl-2,3,5,6-tetrafluorobenzoyl fluoride (**IVB**) (*c.* 5 g, 18 mmol) in CFC113 (50 ml). On completion of the vigorous reaction, ethyl acetate was added and the mixture was washed with water. Evaporation of volatiles from the organic phase left a solid residue (7.5 g) which was recrystallised from ethanol to give the title compound (5.53 g), m.p., 235–237 °C. GLC analysis (programme 1) showed a single peak eluting at 11.6 min. For NMR data see Table 2. MS *m/z*: 351 (83%, M^+); 259 (100); 209 (5); 192 (18); 176 (20); 148 (12); 136 (5); 117 (5); 92 (26); 77 (7); 65 (28). IR (KBr) $\bar{\nu}$: 3254 (m); 3200 (w); 3140 (w); 3084 (w); 1695 (sh); 1672 (s); 1602 (m); 1560 (m); 1494 (s); 1480 (sh); 1442 (s); 1332 (m); 1314 (w); 1290 (w); 1266 (w); 1226 (m); 1198 (w); 992 (s); 882 (w); 792 (m); 772 (w); 758 (m); 740 (w); 696 (w); 612 (s) cm^{-1}.

2,3,5,6-Tetrafluorobenzenesulphonyl fluoride (VII)

A mixture of 4-fluorosulphonyl 2,3,5,6-tetrafluorobenzoic acid (**VIA**) (5.5 g, 19.9 mmol) and dimethyl sulphoxide (2,75 g, 35.3 mmol) was heated at 100 °C for 2 h during which time gas was evolved. The mixture was washed with water, dried ($MgSO_4$) and distilled to give the title compound (2.96 g), b.p., *c.* 53–55 °C/0.3 mbar, which on GLC analysis (programme 2) eluted at 3.0 min. For NMR data see Table 1. Combined GLC–MS and GLC–IR gave *m/z* 232 (100%, M^+); 168 (35); 149 (55); 137 (43); 99 (68); 93 (6); 80 (8); 75 (9); 69 (10); 67 (8), and IR $\bar{\nu}$ 1513 (s); 1454 (w); 1390 (w); 1265 (s); 1219 (w); 1187 (w); 1145 (w); 940 (w); 897 (w); 867 (w); 802 (m); 613 (m) cm^{-1}. IR (film) $\bar{\nu}$: 3086 (w); 1618 (w); 1510 (s); 1434 (s); 1390 (m); 1264 (s); 1212 (s); 1188 (m); 1142 (w); 942 (s); 904 (m); 876 (m); 798 (m) cm^{-1}.

Methyl 4-chlorosulphonyl-2,3,5,6-tetrafluorobenzoate (VIIIA)

Dry methanol (2 ml) was added slowly to 4-chlorosulphonyl-2,3,5,6-tetrafluorobenzoyl chloride (**IVA**) (4.30 g, 13.9 mmol) and the mixture was stirred at room temperature for 30 min. Volatiles were removed under reduced pressure affording a solid (4.5 g) which was purified either by distillation (bath temp. 200 °C/0.5 mbar pressure) or by recrystallisation from hexane to give the title compound (2.1 g), m.p., 55–57 °C. GLC analysis (programme 2) showed a single broad peak eluting at 6.9 min. For NMR data see Table 1. Combined GLC–MS gave *m/z* 308 (30%); 307 (7); 306 (78, M^+); 277 (35); 275 (93); 271 (100, P^+); 213 (16); 211 (53); 207 (44); 192 (36); 176 (88); 148 (83); 129 (11); 117 (28); 105 (12); 98 (44); 79 (17); 59 (70). IR (film) $\bar{\nu}$: 2962 (w); 1738 (s); 1484 (s); 1436 (m); 1396 (s); 1310 (s); 1260 (m); 1236 (m); 1176 (s); 1016 (s); 996 (s); 920 (w); 842 (m); 810 (m); 754 (m); 700 (m) 622 (m) cm^{-1}.

4-Chlorosulphonyl-2,3,5,6-tetrafluorobenzanilide (VIIIB)

A solution of aniline (0.50 g, 5.4 mmol) and triethylamine (0.54 g, 5.4 mmol) in ether (5 ml) was added dropwise to 4-chlorosulphonyl-2,3,5,6-

tetrafluorobenzoyl chloride (**IVA**) (1.65 g, 5.3 mmol) in ether (15 ml) at 0 °C. The mixture was allowed to warm to room temperature, stirred for 1 h and washed with water. Evaporation of the solvent afforded a solid (2.03 g) which was recrystallised from toluene/hexane to give the title compound. For NMR data see Table 2. MS *m/z* 367 (100%, M^+); 275 (75); 211 (18); 192 (20); 176 (53); 148 (36); 94 (62); 92 (34); 77 (13); 65 (54). IR (KBr) $\tilde{\nu}$: 3246 (m); 3140 (m); 3074 (m); 1666 (s); 1606 (m); 1562 (s); 1480 (s); 1446 (m); 1398 (m); 1336 (s); 1310 (m); 1290 (m); 1262 (m); 1208 (w); 1182 (m); 990 (s); 876 (w); 772 (w); 752 (m); 690 (w) cm^{-1}.

*Ethylene glycol bis-(4-fluorosulphonyl)-2,3,5,6-tetrafluorobenzoate (**IX**)*

Dry ethylene glycol (0.75 g, 82.7 mmol) was added to a solution of 4-fluorosulphonyl-2,3,5,6-tetrafluorobenzoyl fluoride (**IVB**) (*c.* 4.2 g, 15 mmol) in CFC113 (20 ml) and the mixture was stirred under dry nitrogen for 18 h. The solvent was removed under reduced pressure and the solid residue was recrystallised from ethanol to give the title compound (1.86 g). The product eluted as a single peak at 27.3 and 4.9 min on GLC (programme 1) and HPLC (1,2-dichloroethane solvent flowing at 1 ml min^{-1}), respectively. For NMR data see Table 1. MS *m/z*: 578 (7%, M^+); 303 (8); 259 (100); 243 (5); 209 (5); 192 (13); 176 (22); 148 (14); 117 (6); 98 (6); 64 (12); 44 (16). IR (KBr) $\tilde{\nu}$: 1736 (s); 1508 (s); 1482 (s); 1446 (w); 1435 (w); 1346 (m); 1304 (s); 1262 (w); 1206 (s); 1036 (m); 996 (m); 868 (w); 794 (m); 708 (w); 612 (s) cm^{-1}.

*Methyl 3-*N*-phenylamino-4-fluorosulphonyl-2,5,6-trifluorobenzoate (**X**)*

A mixture of methyl 4-fluorosulphonyl-2,3,5,6-tetrafluorobenzoate (**VIB**) (0.85 g, 2.9 mmol), triethylamine (0.3 g, 3.0 mmol) and aniline (0.5 g, 5.4 mmol) in dichloromethane (10 ml) was stirred at room temperature for 66 h. The mixture was washed with water, dried ($MgSO_4$), concentrated and purified by chromatography (25 g silica, 10% ethyl acetate in hexane as eluent) to give as an orange gum the title compound (0.8 g), which on GLC analysis (programme 2) eluted as a broad peak (92%) at 11.7 min. For NMR data see Table 2. MS *m/z* (direct insertion, probe at 200 °C): 363 (100%, M^+); 343 (11); 332 (11); 312 (11); 248 (28); 220 (57); 193 (12); 77 (36); 59 (26). IR (KBr) $\tilde{\nu}$: 3402 (s); 3044 (w); 2960 (w); 1746 (s); 1596 (m); 1480 (s); 1430 (m); 1414 (m); 1368 (w); 1304 (s); 1256 (m); 1202 (s); 1018 (m); 992 (m); 784 (s) cm^{-1}.

*Methyl 4-*N*-phenylaminosulphonyl-2,3,5,6-tetrafluorobenzoate (**XI**)*

A mixture of methyl 4-chlorosulphonyl-2,3,5,6-tetrafluorobenzoate (**VIIIA**) (1.42 g, 4.6 mmol), triethylamine (0.49 g, 4.9 mmol) and aniline (0.45 g, 4.8 mmol) in dichloromethane (10 ml) was stirred at room temperature for 4 h. Volatiles were removed under reduced pressure, the mixture was washed with water and extracted with ethyl acetate. The residue obtained on evaporation of the solvent was purified by column chromatography (30 g silica, 15% ethyl acetate in hexane as eluent) affording a solid which was

TABLE 2

NMR data for aniline derivatives of 1,4-X−C_6F_n−Y compounds

Structure (Schemes 1 & 2)	Substituent		Solvent	Nucleus	C_6F_4				X(1) COX′	Y(4) SO_2F	Other	NH−C_6H_5			
	X	Y			1 (*J*, Hz)	4 (*J*, Hz)	2/6 (*J*, Hz)	3/5 (*J*, Hz)				1′	4′	2′/6′	3′/5′
IIIB	CONHPh	Cl	CD_3OD	F	–	–	−140.7	−141.7	–	–	–	–	–	–	–
				C	115.5	125.5	[145.5 and 146.0] (247.7, 253.1)		158.1	–	–	139.4	126.9	122.0	130.6
				H	–	–	–	–	–	–	–	–	7.2(t)	7.65(d)	7.37(t)
VIC	CONHPh	SO_2F	DMSO-d_6	F	–	–	−138.0	−133.7	–	74	–	–	–	–	–
				C	–	–	–	–	170.1	–	–	137.2	125.0	119.7	128.8
				H	–	–	–	–	–	–		–	7.2	7.65	7.38
VIIIB	CONHPh	SO_2Cl	DMSO-d_6	F	–	–	−143.2	−137.6	–	–	–	–	–	–	–
				C	128.2	116.4	142.4	142.4	155.6	–	–	137.8	124.4	119.5	128.8
				H	–	–	–	–	–	–	–	–	7.2	7.75	7.5
X	CO_2Me	SO_2F	$CDCl_3$	F	–	–	F2: −115.7 (16) F6: −143.8 (32)	[3-NHPh] F5: −132.9 (32, 20, 16)	–	71.5 (20, 2)	–	–	–	–	–
				C	119.9	114.3	C2: 147.7 [C5, 6: 145.5 and 141.1]	C3: 129.5	159.2	–	53.7 (OCH_3)	141.0	124.2	119.5	129.3
				H	–	–	–	–	–	–	3.95 (OCH_3)	–	7.1	6.9	7.3
XI	CO_2Me	SO_2NHPh	$CDCl_3$	F	–	–	−136.4	−136.4	–	–	–	–	–	–	–
				C	121.7 (14.4)	116.7 (17.1)	[144.1 and 144.7] (*c*.260)	(*c*. 260)	158.9	–	53.7 (OCH_3)	134.7	126.7	121.5	129.8
				H	–	–	–	–	–	–	3.97 (OCH_3)	–	7.17	7.18	7.29
–	NHPh	SO_2F	CD_3OD	F	–	–	−151.1	−137.9	–	74.6	–	–	–	–	–
				C	134.1	101.4 (32.3, d; 14.4, t)	[147.2 and 139.7]					140.8	125.8	122.7	129.8

[a]Square brackets [ ] denote uncertain assignment between signals bracketed.

recrystallised from toluene–hexane to give the title compound (0.76 g), m.p., 108–110 °C, which on GLC analysis (programme 2) eluted after 15.1 min. For NMR data see Table 2. MS *m/z* 363 (60%, M^+); 332 (6); 284 (5); 268 (10); 267 (18); 239 (4); 176 (8); 148 (8); 93 (17); 92 (100); 91 (10); 66 (5); 65 (70). IR (KBr) $\tilde{\nu}$: 3284 (m); 1750 (m); 1724 (s); 1598 (w); 1478 (s); 1438 (w); 1414 (w); 1358 (w); 1318 (s); 1220 (w); 1172 (s); 1016 (m); 992 (m); 938 (m); 842 (w); 804 (w); 760 (m); 696 (m); 642 (w); 604 (s) cm^{-1}.

4-N-phenylamino-2,3,5,6-tetrafluorobenzenesulphonyl fluoride

Aniline (2.0 g, 21.5 mmol) was added to pentafluorobenzenesulphonyl fluoride (0.43 g, 1.7 mmol) and the solution was stirred at 70 °C for 15 min. On cooling, the mixture was taken up in ether and washed with water. Volatiles were removed under reduced pressure affording a crude product which was purified by recrystallisation from ethanol–water to give as plates the title compound (0.4 g), m.p., 118–119 °C. For NMR data see Table 2. GLC analysis (programme 2) showed a single peak eluting at 11.1 min. Under similar conditions the isomer $C_6F_5SO_2NHPh$ elutes at 8.9 min. MS *m/z* (direct insertion, probe 200 °C): 323 (100%, M^+); 303 (7); 240 (16); 239 (14); 221 (25); 220 (16); 190 (5); 77 (14). IR (KBr) $\tilde{\nu}$: 3388 (m); 1634 (m); 1598 (m); 1530 (s); 1508 (s); 1476 (s); 1434 (m); 1420 (s); 1306 (w); 1284 (m); 1236 (s); 1210 (s); 1144 (w); 1114 (m); 994 (s); 884 (m); 788 (s); 758 (s); 726 (w); 700 (w); 668 (w); 618 (s); 602 (s) cm^{-1}.

Results and discussion

4-Sulphotetrafluorobenzoic acid (**I**) can be readily synthesised in two steps from pentafluorobenzoic acid.

In the first step, reaction of pentafluorobenzoic acid with sodium hydrosulphide in aqueous base gives [15] 4-mercaptotetrafluorobenzoic acid. The mole ratio of $C_6F_5CO_2H$:NaSH must be carefully controlled to prevent formation of the by-product, 4,4′-dicarboxy-octafluorodiphenylthioether. An analogous reaction can be effected [16] with pentafluorobenzaldehyde to give 4-mercaptotetrafluorobenzaldehyde. The mercapto-benzoic acid has also been prepared previously by carbonation of the dilithium salt of 2,3,5,6-tetrafluorothiophenol [17, 18] and by reaction of sulphur with the dilithium salt of 2,3,5,6-tetrafluorobenzoic acid [19]. The carbonation method has similarly been used [18] to prepare the *ortho*-mercaptobenzoic acid analogue by starting with 2,3,4,5-tetrafluorothiophenol. The infrared OH stretching frequency of 4-mercaptotetrafluorobenzoic acid has been separately reported [20].

In the second step of the synthesis, oxidation of the 4-mercaptobenzoic acid with acetic acid/hydrogen peroxide affords the *para*-sulphobenzoic acid (**I**). Absolute purification of the 1,4-diacid, particularly from inorganic salts carried through the extraction process, was not achieved.

Derivatives, such as esters or amides, of the sulphobenzoic acids may be conveniently prepared via intermediates in which the acid groups are

activated. A standard approach is to convert the free acids to acid halide, particularly chloride, groups. Such carbonyl- and sulphonyl-chloride groups are usually readily converted to their fluoride analogues by fluoride exchange.

The diacid, dried to constant weight at 60 °C and 0.5 mbar pressure, appeared not to react at room temperature with up to about a 3.5 molar excess of thionyl chloride. This probably reflects consumption of the thionyl chloride by residual water, coupled with limited solubility of the acid in the reaction mixture. Indeed this procedure was found to be ideal for chemically drying the acid in a similar manner to that described by Satori and Bauer [6a] for pentafluorobenzenesulphonic acid. The acid is otherwise difficult to dry by purely physical means, such as heat/vacuum.

However, the diacid **I** behaved differently when treated with a gross excess of thionyl chloride containing DMF. The DMF/$SOCl_2$ couple, which produces dimethylchloroforminium chloride (Me_2NCHCl_2) as the active agent, is a standard method for increasing chlorinating activity particularly for sulphonic acids. Spectral analysis suggested that the product from this reaction, isolated in good yield, was 4-chlorotetrafluorobenzoyl chloride (**IIA**). The 4-chlorotetrafluorobenzoyl moiety was independently confirmed by the preparation of the methyl ester 1,4-$ClC_6F_4CO_2Me$ (**IIIA**) and anilide 1,4-$ClC_6F_4CONHPh$ (**IIIB**) derivatives, respectively.

Using an alternative approach, the diacid chloride 1,4-$ClOCC_6F_4SO_2Cl$ (**IVA**) was produced in good yield by reaction of the *para*-diacid with PCl_5. This parallels the behaviour of the hydrocarbon analogue 1,4-$HO_2CC_6H_4SO_3H$ [21]. However, in a situation analogous to that seen in the $SOCl_2$/DMF reaction, attempted conversion of the diacid chloride **IVA** to the diacid fluoride 1,4-$FOCC_6F_4SO_2F$ (**IVB**) using activated KF in tetraglyme resulted in the extrusion of SO_2 to give 1,4-ClC_6F_4COCl (**IIA**) which, under the reaction conditions, was further converted to 1,4-ClC_6F_4COF (**IIB**) by halogen exchange. The SO_2 extrusion reaction appeared to be most active in the presence of ionic species. For example, 1,4-ClC_6F_4COCl (**IIA**) was produced when the barium salt of the diacid was used in the PCl_5 reaction.

The acid chloride 1,4-ClC_6F_4COCl (**IIA**), produced in the $SOCl_2$/DMF reaction, was readily converted to the benzoyl fluoride analogue 1,4-ClC_6F_4COF (**IIB**) by halogen exchange using sodium fluoride and tetraphenylphosphonium bromide as a phase-transfer agent in tetraglyme. 4-Chloro-2,3,5,6-tetrafluorobenzoic acid has previously been made, for example, by chlorination of the dilithium salt of 2,3,5,6-tetrafluorobenzoic acid [19a]. However 4-chloro-2,3,5,6-tetrafluorobenzoyl halide derivatives do not appear to have been previously reported although *Chemical Abstracts* cite the 2-chloro [22] and 3-chloro [23] isomers, and an unassigned isomer [24], of chloro-tetrafluorobenzoyl fluoride.

The mechanism of the SO_2 extrusion in the above reactions was not investigated. However, such extrusions from activated aromatic sulphonyl compounds are well known, with either radical or ionic mechanisms being implicated. For example, boiling $C_6F_5SO_2Cl$ in 1,3,5-$C_6H_3Cl_3$ in the presence

of $CuCl_2$ catalyst results [25] in the formation, via a proposed homolytic free-radical mechanism, of 2′,4′,6′-$C_6H_2Cl_3-C_6F_5$ with nearly quantitative amounts of SO_2 and HCl being evolved. Reaction of $C_6F_5SO_2Cl$ with C_6F_5H in the presence of SbF_5 at 110 °C gives [26] $(C_6F_5)_2SO_2$ and $C_6F_5-C_6F_5$, the latter compound presumably originating by loss of SO_2 and HCl. Temperature-dependent sulphur dioxide extrusions from partially chlorinated aromatic sulphonyl chlorides and fluorides have been reported by Yakobson *et al.* [27]. Comparable behaviour has been seen [28] in chlorobenzene and chloropyridine sulphonyl fluorides and extrusions have also been reported in the field of purine chemistry [29]. Fluorodesulphonations catalysed by KF have been used [30] in the synthesis of fluorinated aromatic compounds.

Results both from the above and from our contemporaneous work on 1,2-tetrahalosulphobenzoic acid difluoride [31] indicated that conversion of the diacid chloride **IVA** to the diacid fluoride **IVB** by fluoride exchange was not a practical approach due to the susceptibility of the sulphonyl halide group to SO_2 extrusion. This led to a search for an alternative method or reagent for making the diacid fluoride derivative directly from the diacid **I**. One such reagent known [32, 33] to convert both carboxylic and sulphonic acids to their acid fluorides is sulphur tetrafluoride. The functional groups present together with the 'non-reacting' part of the molecule have a significant influence on the conditions needed in SF_4 reactions [34, 35]. It was shown that under controlled stoichiometry, necessitating dry feedstock, the desired products could be produced in good yields and under relatively mild conditions. For example, when employing a 1:2 mole ratio (or lower) of diacid **I** to SF_4, the anticipated diacid fluoride 1,4-$FOCC_6F_4SO_2F$ (**IVB**) was produced, while the use of excess SF_4 resulted in the formation of *para*-perfluorotosyl fluoride 1,4-$CF_3C_6F_4SO_2F$ (**V**).

Carbonyl (−COHal) and sulphonyl ($-SO_2Hal$) halide groups have widely differing reactivities, the former being much more susceptible to nucleophilic attack than the latter. Advantage can be taken of the differential reactivity in the preparation of derivatives. For example, on exposure to water the diacid fluoride 1,4-$FOCC_6F_4SO_2F$ (**IVB**) was converted to the half-acid 1,4-$HO_2CC_6F_4SO_2F$ (**VIA**), which was shown to decarboxylate readily in hot DMSO affording 2,3,5,6-tetrafluorobenzenesulphonyl fluoride, 1,4-$HC_6F_4SO_2F$ (**VII**). In the same manner, reaction of either the diacid fluoride or chloride 1,4-$XOCC_6F_4SO_2X$ (**IVA**, X = Cl or **IVB**, X = F) with methanol rapidly converted the carbonyl halide group (−COX) to the methyl ester ($-CO_2Me$) leaving the sulphonyl halide group intact, affording respectively 1,4-$MeO_2CC_6F_4SO_2F$ (**VIB**) or 1,4-$MeO_2CC_6F_4SO_2Cl$ (**VIIIA**). Likewise, on reaction with equimolar amounts of aniline the diacid fluoride or chloride were converted to, principally, their respective anilides 1,4-$PhNHOCC_6F_4SO_2F$ (**VIC**) or 1,4-$PhNHOCC_6F_4SO_2Cl$ (**VIIIB**), again with the sulphonyl halide group remaining intact. The ethyl ester 1,4-$EtO_2CC_6F_4SO_2F$ may be similarly made and was formed when commercial chloroform containing small amounts of ethanol was used as a solvent for the diacid fluoride. Analogous reaction of the diacid fluoride with ethylene glycol gave 1,4-$[CH_2OCOC_6F_4SO_2F]_2$ (**IX**).

In addition to the widely differing reactivities of the carbonyl and sulphonyl halide groups, there is a difference in reactivity between chloride and fluoride derivatives of each, the chloride derivatives being more reactive than their fluoride counterparts. For example, on the controlled addition of sodium methoxide to a mixture of 4-chloro-tetrafluorobenzoyl chloride and fluoride (1,4-ClC_6F_4COX; **IIA**, X=Cl or **IIB**, X=F) the chloride derivative reacted first to give the methyl ester 1,4-$ClC_6F_4CO_2Me$ (**IIIA**).

The behaviour is much more pronounced in the case of the sulphonyl halides where the difference in reactivities leads to competition between nucleophilic aromatic substitution and condensation reactions. This may be illustrated by the reaction of aniline with the model compounds pentafluorobenzenesulphonyl chloride and fluoride. Condensation of $C_6F_5SO_2Cl$ with an excess of aniline gave, as the major product, the sulphonamide $C_6F_5SO_2NHPh$. In contrast, the sulphonyl fluoride group is so much less reactive than the sulphonyl chloride that similar treatment of $C_6F_5SO_2F$ with an excess of aniline produced, by nucleophilic aromatic substitution, predominantly 1,4-$PhNHC_6F_4SO_2F$. This molecule does not appear to have been previously cited in *Chemical Abstracts*.

The differential reactivity of the sulphonyl chloride/fluoride groups is further illustrated by the reaction of the methyl ester derivatives, 1,4-$MeO_2CC_6F_4SO_2X$ (X=Cl or F), with equimolar amounts of aniline. Such treatment of the sulphonyl fluoride **VIB** afforded as the major product methyl 3-*N*-phenylamino-4-fluorosulphonyl-2,5,6-trifluorobenzoate (**X**). In contrast, the sulphonyl chloride produces as the major compound the ester-sulphonamide derivative 1,4-$MeO_2CC_6F_4SO_2NHPh$ (XI).

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