# Poly(arylene ether sulphones) by polyetherification: 1. Synthesis of halogenophenols*

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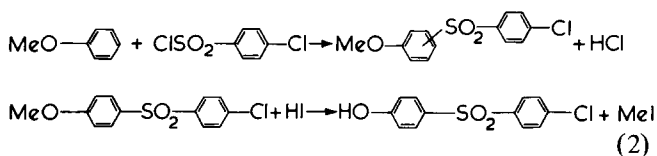*(Received 22 November 1976)*

Several 4-halogenophenylsulphonylphenols, useful as intermediates for the synthesis of poly(arylene ether sulphones), have been prepared by partial hydrolysis of the corresponding dihalides and/or by the reaction of 4-halogenoarylsulphonyl chlorides with diaryl carbonates under Friedel–Crafts conditions followed by hydrolysis of the sulphonylated carbonates. The novel reagent, diphenyl carbonate-4,4'-disulphonyl chloride, has been prepared by chlorosulphonylation of diphenyl carbonate and used to introduce the 4-hydroxyphenylsulphonyl group into aryl halides, thus providing a third general route to the halogeno phenols. 4-Fluoro-3'-hydroxydiphenyl sulphone and the 4-fluoro-2'-hydroxy derivative have been synthesised by classical procedures.

INTRODUCTION

The alkali metal derivatives of phenols containing 4-halogenophenylsulphonyl groups are useful intermediates for the synthesis of poly(arylene ether sulphones) by reactions such as equation $(1)^{1,2}$.

$$KO-\bigcirc-SO_2-\bigcirc-Cl \longrightarrow \ {\rm [}O-\bigcirc-SO_2-\bigcirc {\rm]} + KCl \quad (1)$$
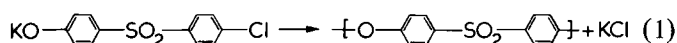
Halogenophenols of this type received little attention prior to their use as polymer intermediates and the synthetic methods available, e.g. reaction sequence $(2)^3$, were laborious and not suited to large scale operation.

$$MeO-\bigcirc + ClSO_2-\bigcirc-Cl \longrightarrow MeO-\bigcirc \overset{SO_2-\bigcirc-Cl}{} + HCl$$

$$MeO-\bigcirc-SO_2-\bigcirc-Cl + HI \longrightarrow HO-\bigcirc-SO_2-\bigcirc-Cl + MeI \quad (2)$$

With the emergence of poly(arylene ether sulphones) as potentially important new thermoplastics we became interested in the preparation of intermediates for these polymers and this paper describes methods developed in our laboratories for synthesis of the halogenophenols. Certain halogenophenols in which the functional groups were not both in the p,p'-orientation to the sulphone linkage were required for structural investigations and the synthesis of these by classical procedures is also briefly described.

RESULTS AND DISCUSSION

### Hydrolysis of halogenated derivatives of diphenylsulphone

Sulphonation and arylsulphonylation of halogenated benzenes occurs predominantly para to halogen so that 4-chlorobenzenesulphonyl chloride is obtained by treating chlorobenzene with chlorosulphonic acid[4] and can then be used to sulphonylate chlorobenzene under Friedel–Crafts

conditions, when the yield of 4,4'-dichlorodiphenyl sulphone is 89% (reaction 3)[5].

$$Cl-\bigcirc-SO_2Cl + \bigcirc-Cl \longrightarrow Cl-\bigcirc-SO_2-\bigcirc-Cl + HCl \quad (3)$$
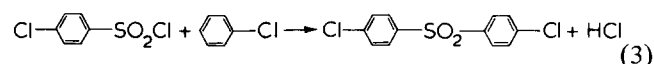
Dichlorodiphenyl sulphone can also be obtained by treating chlorobenzene with sulphur trioxide and methyl pyrosulphate (from methyl sulphate and SO_3) when again *para* substitution predominates and the 4,4'-dichloride is obtained in 90% yield (reaction 4)[6].

$$2\bigcirc-Cl + SO_3 + (MeOSO_2)_2O \longrightarrow Cl-\bigcirc-SO_2-\bigcirc-Cl + 2MeOSO_2OH \quad (4)$$
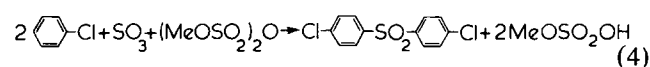
Thus, 4,4'-dihalogenodiphenyl sulphones (I), are readily accessible and it has been shown that the reaction of these compounds with potassium hydroxide in aqueous dimethyl sulphoxide (DMSO) proceeds in two distinct stages, reaction (5) (R = H) going virtually to completion without significant hydrolysis to the bisphenoxide[1,7].

$$Hal-\bigcirc-SO_2-\bigcirc-Hal + 2KOH \longrightarrow Hal-\bigcirc-SO_2-\bigcirc-OK + KHal \quad (5)$$
$$\overset{R}{}\ (I)\quad \overset{R}{} \qquad \overset{R}{}\ (II)\quad \overset{R}{}$$
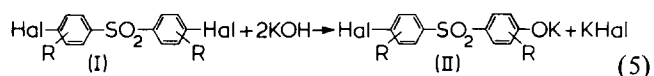
Halogeno substituents oriented *meta* (R = *m*-Cl in I) to the sulphone group do not interfere, but when R is *o*-Cl a mixture of products is obtained. A full discussion of the factors governing the rates of halide displacement from halogenated derivatives of diphenylsulphone has already been given[8] so that the data in this paper are concerned only with preparative details.

Reaction (5) goes to completion under mild conditions (*Table 1*) and the chlorophenols separate out either as solids or as oils (which solidify on standing) on pouring the total reaction product into dilute hydrochloric acid. Yields of crude product are high and losses on recrystallization relatively small, except for R = *o*-Cl when the crude product contains unreacted tetrachloride plus 4,4'-dichloro-2,2'-dihydroxydiphenyl sulphone as well as the required trichlorophenol. Initially the reaction mixture forms two layers and vigorous stirring is required until

Table 1 Preparation of halogenophenols by reaction (5)

Reactant, I		Reaction conditions			Yield of halogenophenols		
Hal	R	Temperature (°C)	Time (h)	[I]/1.DMSO (mol)	Crude (%)	Recryst. (%)	M.p. (°C)
Cl	H	110	21	1.0	85	72	150
F	H	60	24	1.0	80	71	155
Cl	m-Cl	100	2	0.56	98	58	196–197
Cl	o-Cl	100	4	0.38	–	23	139–140

Table 2 Sulphonylation of aryl carbonates

Reactants	Reaction conditions			Halogenophenol[†]		Yield[≠]
	Temperature (°C)	Time (h)	HCl evolved* (%)	Structure	M.p. (°C)	(%)
(⬡–O–)₂CO, F–⬡–SO₂Cl	120–160	8	85	F–⬡–SO₂–⬡–OH	156	70
(⬡–O–)₂CO, Cl–⬡–SO₂Cl	150	5	86	Cl–⬡–SO₂–⬡–OH	150	55
(⬡–⬡–O–)₂CO, Cl–⬡–SO₂Cl	120	4	87	Cl–⬡–SO₂–⬡–⬡–OH	269–271	70
(naphthyl–O–)₂CO, F–⬡–SO₂Cl	115	3	90	F–⬡–SO₂–naphthyl–OH	153–154	37
(naphthyl–O–)₂CO, ClSO₂–naphthyl–Cl	125	1	70	Cl–naphthyl–SO₂–naphthyl–OH	280–281	61

* Expressed as % of that expected theoretically; [†] isolated on hydrolysis of the carbonate; [≠] yield of purified product, m.p. as quoted, based on diaryl carbonate used

the liquid plase becomes homogenous.

Fluorine is displaced from 4-halogenophenylsulphonyl groups by hydroxyl ions over 100 times faster than chlorine[8], and this difference in reactivity can be used to obtain a chlorophenol, via the potassium salt, V, from the chlorofluoro derivative, IV. The full synthesis of V, which can be used for the preparation of poly(arylene ether sulphones) with particularly high values of T_g, is shown in reaction sequence (6).

$$
\bigcirc\!\!-\!\!\bigcirc + Cl\!-\!\!\bigcirc\!\!-SO_2Cl \longrightarrow \bigcirc\!\!-\!\!\bigcirc\!\!-SO_2\!\!-\!\!\bigcirc\!\!-Cl + HCl
$$
(III)

$$
(III) + F\!-\!\!\bigcirc SO_2Cl \longrightarrow F\!-\!\!\bigcirc\!\!-SO_2\!\!-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-SO_2\!\!-\!\!\bigcirc\!\!-Cl + HCl
$$
(IV)

$$
(IV) + 2KOH \longrightarrow KO\!-\!\!\bigcirc\!\!-SO_2\!\!-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-SO_2\!\!-\!\!\bigcirc\!\!-Cl + KF
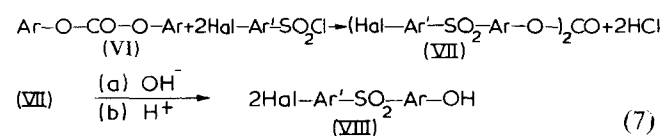$$
(V)
(6)
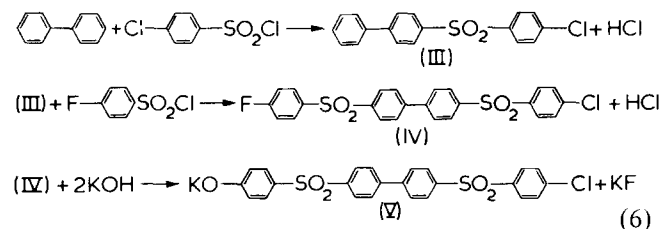
4-Chlorophenylsulphonylation of diphenyl with one molar equivalent of sulphonyl chloride gives a good yield of III and 4-fluorophenylsulphonylation of III occurs mainly in the p' position so that the overall yield of IV is 60% (after recrystallization) based on the amount of diphenyl employed. Presumably, when the 4-chlorophenylsulphonyl group is attached to one ring in diphenyl (as in III) it reduces the reactivity of the

other and helps to direct further sulphonylation towards the p' position. Thus, formation of the bis-4-chlorophenylsulphonyl compound is minimized during the first Friedel–Crafts reaction and a high yield of IV is obtained in the second. An analogous situation obtains for the nitration of diphenyl where mononitration occurs faster than dinitration and p-nitrodiphenyl is nitrated predominately in the p'-position[9].
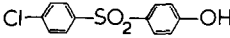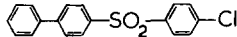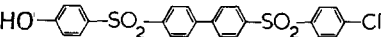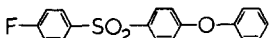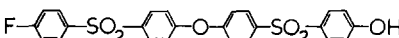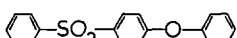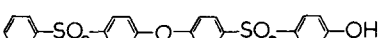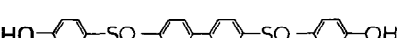
Sulphonylation of diaryl carbonates

Nuclear sulphonylation of phenols is not possible under Friedel-Crafts conditions unless the phenolic hydroxyl is protected, e.g. by etherification as in reaction sequence (2). We have found that the carbonate linkage in bisarylcarbonates (VI) acts as a protecting group during sulphonylation of aromatic nuclei and that the sulphonylated phenols, VIII, are then easily obtained by hydrolysis of the corresponding carbonates (reaction sequence 7).

$$
Ar\!-\!O\!-\!CO\!-\!O\!-\!Ar + 2Hal\!-\!Ar'\!-\!SO_2Cl \rightarrow (Hal\!-\!Ar'\!-\!SO_2\!-\!Ar\!-\!O\!-)_2CO + 2HCl
$$
(VI) (VII)

$$
(VII) \xrightarrow[\text{(b) } H^+]{\text{(a) } OH^-} 2Hal\!-\!Ar'\!-\!SO_2\!-\!Ar\!-\!OH
$$
(VIII)
(7)

Sulphonylation proceeds smoothly at 110° to 150°C in nitrobenzene solution in the presence of small quantities

Table 3 Sulphonylation with diphenyl carbonate disulphonyl chloride

Substrate	Reaction conditions			Phenolic product*		
	Temperature ($^\circ$C)	Time (h)	HCl evolved (%)	Structure	M.p. ($^\circ$C)	Yield (%)
⬡—Cl	150	4	60	Cl—⬡—SO$_2$—⬡—OH	149–150	60
⬡—⬡—SO$_2$—⬡—Cl	140	2–6	80	HO—⬡—SO$_2$—⬡—⬡—SO$_2$—⬡—Cl	158, 252[†]	48
F—⬡—SO$_2$—⬡—O—⬡	110	7	80	F—⬡—SO$_2$—⬡—O—⬡—SO$_2$—⬡—OH	225–228	33
⬡—SO$_2$—⬡—O—⬡	110	24	91	⬡—SO$_2$—⬡—O—⬡—SO$_2$—⬡—OH	165–167	40
⬡—⬡	150	4	80–90	HO—⬡—SO$_2$—⬡—⬡—SO$_2$—⬡—OH	250–251	–

* Isolated on hydrolysis of the carbonate; [†] Dimorphic

(0.01 mol/mol sulphonyl chloride used) of anhydrous ferric chloride. The sulphonylated carbonates VII, crystallize from the reaction mixture on cooling or on precipitation into methanol, and the hydrolysis of these compounds occurs rapidly on treatment with alcoholic potassium hydroxide. Halogeno phenols prepared by this route are listed in *Table 2*.

The stability of the carbonate linkage under Friedel–Crafts conditions suggested that it might resist the more strongly acidic conditions required for chlorosulphonation with chlorosulphonic acid. Thus, we found that treatment of diphenyl carbonate with 5 mol of chlorosulphonic acid gave the 4,4'-disulphonyl chloride, IX, in 60% yield. This novel reagent (a solid m.p. 149°–150°C) provides a means of introducing the 4-hydroxyphenylsulphonyl group into molecules by the generalized reaction sequence (8) and has been used by us to perform the preparations summarized in *Table 3*.

$$(ClSO_2\text{—}⬡\text{—}O\text{—})_2CO + 2ArH \xrightarrow{FeCl_3} (Ar\text{—}SO_2\text{—}⬡\text{—}O\text{—})_2CO + 2HCl$$
$$\text{(IX)} \qquad\qquad\qquad\qquad \text{(X)}$$

$$(ArSO_2\text{—}⬡\text{—}O\text{—})_2CO \xrightarrow[\text{(b) H}^+]{\text{(a) OH}^-} 2Ar\text{—}SO_2\text{—}⬡\text{—}OH \qquad (8)$$
$$\text{(XI)}$$

The Friedel–Crafts reaction proceeds readily in the presence of small quantities of FeCl$_3$ using nitrobenzene as the solvent, and the intermediate carbonates, X, are cleaved readily by potassium hydroxide to give the phenolic products, XI, on acidification. It is interesting to note that the carbonate linkage is substantially inert under the highly acidic conditions of the sulphonylation reactions, presumably due to the absence of nucleophilic reagents e.g. water, from the reaction media. The carbonate linkage does not deactivate the ferric chloride used as the Friedel–Crafts condensing agent so that this can be used in catalytic quantities as was found by Huissman[10] for the reaction of sulphonyl chlori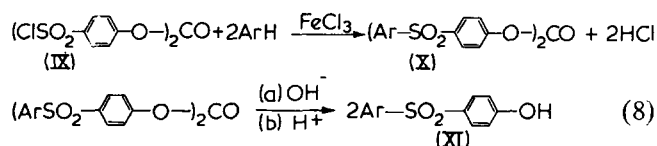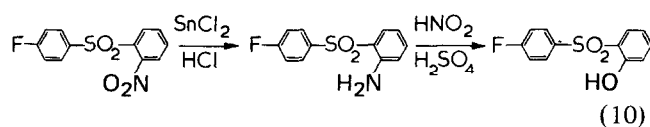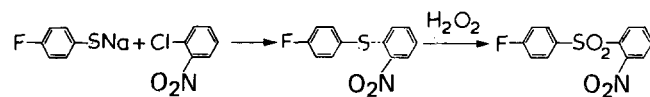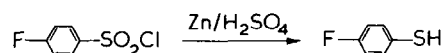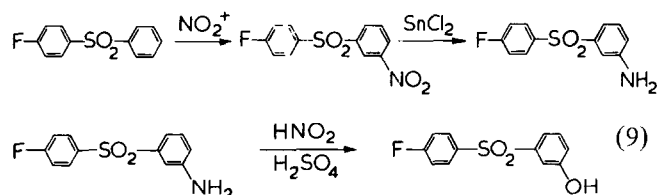des with aromatic hydrocarbons. The only identifiable products isolated from the arylsulphonylation and the chlorosulphonylation of diphenyl carbonate are those in which the sulphone group is positioned *para* to the carbonate linkage and although no attempts were made to isolate isomeric products, the relatively high yields of purified *para*-isomers obtained suggests that the carbonate group directs sulphonylation predominantly towards the *para*-position. In this respect

the carbonate group behaves like a halogeno substituent and this analogy is retained with the α-substituted naphthalenes as it appears from our data that the carbonate of α-naphthol undergoes sulphonylation predominantly in the *para*-position of the α-substituted ring as is the case with α-chloronaphthalene[11]. No accurate rate measurements were made, but the preparative conditions required to sulphonylate the aryl carbonates were comparable to those required for sulphonylating the corresponding halides.

Classical syntheses

4-Fluoro-3'-hydroxydiphenylsulphone and the 4-fluoro-2'-hydroxy isomer were synthesised as shown in reaction schemes (9) and (10). These laborious multistage syntheses are in marked contrast to the simple procedures described above for preparing the 4,4'-isomer.

$$F\text{—}⬡\text{—}SO_2\text{—}⬡ \xrightarrow{NO_2^+} F\text{—}⬡\text{—}SO_2\text{—}⬡_{NO_2} \xrightarrow{SnCl_2} F\text{—}⬡\text{—}SO_2\text{—}⬡_{NH_2}$$

$$F\text{—}⬡\text{—}SO_2\text{—}⬡_{NH_2} \xrightarrow[H_2SO_4]{HNO_2} F\text{—}⬡\text{—}SO_2\text{—}⬡_{OH} \qquad (9)$$

$$F\text{—}⬡\text{—}SO_2Cl \xrightarrow{Zn/H_2SO_4} F\text{—}⬡\text{—}SH$$

$$F\text{—}⬡\text{—}SNa + Cl\text{—}⬡_{O_2N} \longrightarrow F\text{—}⬡\text{—}S\text{—}⬡_{O_2N} \xrightarrow{H_2O_2} F\text{—}⬡\text{—}SO_2\text{—}⬡_{O_2N}$$

$$F\text{—}⬡\text{—}SO_2\text{—}⬡_{O_2N} \xrightarrow[HCl]{SnCl_2} F\text{—}⬡\text{—}SO_2\text{—}⬡_{H_2N} \xrightarrow[H_2SO_4]{HNO_2} F\text{—}⬡\text{—}SO_2\text{—}⬡_{HO} \qquad (10)$$

EXPERIMENTAL

Hydrolysis of halogenated derivatives of diphenyl sulphone

The syntheses listed in *Table 1* were performed by procedures analogous to that described below for 4-fluoro-4'-hydroxydiphenyl sulphone.

4-Fluoro-4'-hydroxydiphenyl sulphone. 4,4'-Difluoro-diphenyl sulphone (1017 g, 4.0 mol), 50% aqueous KOH

(918 g, 8.0 mol) and dimethyl sulphoxide (4 l) were heated for 24 h at 60°C under nitrogen in a stainless steel vessel fitted with an efficient stirrer, and then the product was poured into iced water (10 l). After filtration to remove unreacted difluoride, the solution was acidified with concentrated hydrochloric acid to give an oil which crystallized on standing. This solid was filtered off, and washed with water in a laboratory blender. It was then dissolved in methanol (3 l) treated with activated charcoal and the filtered solution poured into iced water. The solid so obtained was dried and then distilled at 0.2 mm to give crude 4-fluoro-4'-hydroxydiphenyl sulphone (812 g) b.p. 242°C. Recrystallization from toluene gave the pure fluorophenol, (712 g, 70% yield) m.p. 154°–5°C; Szmant and Suld[3] report m.p. 157°–8°C.

4-(4-Chlorophenylsulphonyl)-4'-(-4-hydroxyphenylsulphonyl) diphenyl. A mixture of diphenyl (308 g, 2.0 mol), 4-chlorobenzenesulphonyl chloride (422 g, 2.0 mol) and nitrobenzene (0.5 l) was heated under nitrogen with stirring to 110°C. Anhydrous ferric chloride, 4 g, was added and stirring continued at 110°C until evolution of HCl ceased. The product was poured into methanol (2 l) and the precipitate filtered off, washed twice with methanol (0.5 l) containing acetyl acetone (5 cm³) to remove iron, washed once with methanol and dried. The crude product (542 g, 80% yield) had m.p. 167°–8°C. Recrystallization from acetic acid gave (after decolourizing with charcoal) white needles of 4-(4-chlorophenylsulphonyl) diphenyl, III, (400 g, 62% yield) m.p. 171°–3°C. Found: C, 66.6; H, 4.0; Cl, 10.8%. $C_{18}H_{13}SO_2Cl$ required C, 65.7; H, 4.0; Cl 10.8%.

A mixture of III (162 g, 0.5 mol) redistilled 4-fluorobenzenesulphonyl chloride (105 g, 0.54 mol), nitrobenzene (0.35 l) and anhydrous ferric chloride (2 g) were heated to 110°C and stirred at this temperature until evolution of HCl ceased. The product was poured into methanol (1 l) and the precipitate washed with methanol containing a little acetyl acetone and dried. Recrystallization from acetic acid (decolourizing with charcoal) gave 4-(4-fluorophenylsulphonyl)-4'-(4-chlorophenylsulphonyl) diphenyl, IV, as white needles (163 g, 68% yield) m.p. 235°–238°C. Found: C, 59.5; H, 3.2; Cl, 7.8; F, 3.9%. $C_{24}H_{16}O_4S_2FCl$ requires C, 59.2; H, 3.3; Cl, 7.3; F, 3.9%.

IV (49 g, 0.1 mol) was dissolved in dimethyl sulphoxide (0.51 l) by heating to 110°C under nitrogen in a stainless steel vessel. Aqueous KOH (0.2 mol as 50% solution) was added and the mixture stirred vigorously while the temperature was increased to 125°C during 5.5 h. The mixture was then cooled and poured into dilute hydrochloric acid and the white precipitate filtered off and washed with water. Recrystallization of the dried solid from acetic acid gave white needles of 4-(4-chlorophenylsulphonyl)-4'-(4-hydroxyphenylsulphonyl)diphenyl m.p. 253°C. Found: C, 59.6; H, 3.2; Cl, 7.5%. $C_{24}H_{17}S_2O_5Cl$ required C, 59.5; H, 3.4; Cl, 7.4%.

Sulphonylation of diaryl carbonates

The syntheses listed in *Table 2* were performed by procedures analogous to those described below for 1-hydroxy-4-(4-fluorophenylsulphonyl) naphthalene and 4-(4-chlorophenyl sulphonyl)-4'-hydroxy diphenyl.

1-Hydroxy-4-(4-fluorophenylsulphonyl) naphthalene. Di(1-naphthyl carbonate) m.p. 129°–130°C, (Reverdim[12] reports m.p. 130°C) was prepared by ester interchange from 1-naphthol and diphenyl carbonate using sodium hydride as

catalyst. The carbonate (157 g, 0.5 mol), 4-fluorobenzenesulphonyl chloride (195 g, 1.0 mol) and nitrobenzene (140 cm³) were heated with stirring to 115°C for 3 h when HCl evolution virtually ceased. Nitrobenzene (~110 ml) was distilled out at ~14 mmHg pressure and the residue washed with methanol in a laboratory blender to give the crude sulphonylated carbonate (a sample crystallized from toluene had m.p. 233°–236°C). This was slurried in methanol (3 l) and treated at room temperature with 50% aqueous KOH (220 g, 2 mol). The solution so obtained was acidified with concentrated hydrochloric acid to give the crude phenol which was dried, sublimed and then recrystallized from methanol to give the pure fluorophenol (110 g, 37% yield) m.p. 152°–4°C. Found: C, 63.3; H, 3.3; F, 5.8; S, 10.2%. $C_{12}H_{11}FO_3S$ requires C, 63.6; H, 3.7; F, 6.3; S, 10.6%. The n.m.r. spectrum (220 MHz) was recorded and interpreted thus, chemical shifts being recorded as δ ppm from tetramethylsilane.
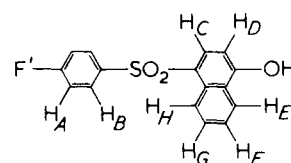
δ (CDCl₃) 8.59 (dd, H_H, J_{GH} 8.5 Hz, J_{FH} 1.5 Hz); 8.41 (d, H_C, J_{CD} 8.5 Hz); 8.31 (dd, H_E, J_{EF} 8 Hz, J_{EG} 1.5 Hz); 7.95 (q, 2H$_B$, J_{AB} 9 Hz, $J_{F'B}$ 5 Hz); 7.58 (td, H_G and H_F, J_{GF} 9 Hz); 7.08 (t, 2H$_A$, $J_{F'A}$ 9 Hz); 6.88 (d, H_D) ppm.

4-(4-Chlorophenylsulphonyl)-4'-hydroxydiphenyl. The carbonate of 4-hydroxydiphenyl (293 g, 0.80 mol: m.p. 184°C; prepared from the phenol and diphenyl carbonate by ester interchange using sodium hydride as catalyst), 4-chlorobenzenesulphonyl chloride (371 g, 1.76 mol), nitrobenzene (0.4 l) and anhydrous ferric chloride were stirred together under nitrogen at 120°C for 2 h when the evolution of HCl was complete. Methanol (0.5 l) was added and the mixture stirred vigorously. The solid product was filtered off, washed with methanol and then dried under vacuum. A small portion, recrystallized from o-dichlorobenzene had a m.p. 284°–288°C. Found: C, 62.6, H, 3.3; S, 8.4; Cl, 9.8%. $C_{37}H_{24}O_7S_2Cl_2$ requires C, 62.1; H, 3.4; S, 8.9; Cl, 9.9%. The remainder (570 g) was stirred under reflux with aqueous KOH (3.84 mol) and ethanol (0.75 l) for 2.5 h. The pasty product so obtained was dissolved in cold methanol, decanted off from solids and acidifed slowly with a 1:1 mixture of water and concentrated hydrochloric acid to give a white solid which was filtered off, washed with methanol and dried under vacuum. Recrystallization twice from dimethylformamide containing a little water gave 4-(4-chlorophenylsulphonyl)-4'-hydroxydiphenyl (313 g, 57% yield) m.p. 269°–271°C. Found: C, 62.9; H, 3.8; Cl, 10.1%. $C_{18}H_{13}ClSO_3$ requires C, 62.6; H, 3.8; Cl, 10.4%.

Synthesis and use of diphenyl carbonate-4,4'-disulphonyl chloride (IX)

Synthesis of IX. Diphenyl carbonate (1070 g, 5 mol) was dissolved in chloroform (1 l) and chlorosulphonic acid (1720 g, 25 mol) added during 9 h while the reaction mixture was stirred vigorously and cooled to keep the temperature below 30°C. The product was allowed to stand overnight; poured onto ice and extracted with chloroform. Evaporation of the chloroform gave IX (1235 g, 60% yield), m.p. 148°–150°C. Found: C, 37.7; H, 1.8; Cl, 16.0%. $C_{13}H_8O_7S_2Cl_2$ requires C, 37.9; H, 1.8; Cl, 17.3%.

Synthesis of 4-(4-chlorophenylsulphonyl)-4'-(4-hydroxy-phenylsulphonyl) diphenyl

4-(4-Chlorophenylsulphonyl)diphenyl (80.5 g, 0.245 mol), the disulphonyl chloride, IX, (50 g, 0.123 mol), nitrobenzene (250 ml) and anhydrous ferric chloride (~1.0 g) were heated to 140°–150°C with stirring for 9 h. The product was then poured into methanol and the solid filtered off, washed with methanol containing acetyl acetone and dried to give the crude sulphonylated carbonate (56 g, 49% yield). A part of this product (44 g) was heated under reflux with ethanolic potassium hydroxide (200 cm³ ethanol and 12 g KOH) for 1 h, cooled, filtered, and poured into dilute hydrochloric acid. The precipitate was washed with water and recrystallized from isopropanol to give the chlorophenol (35 g, 95% yield) m.p. 159°–161°C and 253°–5°C. Differential thermal analysis of this melting process indicates that the chlorophenol exists in two crystallographic forms the one m.p. 159°–161°C being irreversibly converted to the other (m.p. 253°–5°C) via an exothermic process at 169°C.

Synthesis of 4-(4-fluorobenzenesulphonyl)-4'-(4-hydroxy-benzenesulphonyl)diphenyl ether (XII)

Potassium phenoxide was prepared under nitrogen from phenol (94 g, 1.0 mol) and 1 mol of aqueous potassium hydroxide in dimethyl sulphoxide (0.8 l) solution. After removal of water by azeotropic distillation with benzene, 4,4'-difluorodiphenyl sulphone (254 g, 1.0 mol) was added and the stirred mixture maintained at 60°C for 24 h. The product was filtered, poured into iced water and extracted with ether. After drying, the extract was distilled to remove ether and the residual oil distilled at 0.5 mmHg to give two fractions; the first (27 g) b.p. 141°–153°C was unreacted difluoride and the second (132 g) b.p. 215°C was 4-fluoro-4'-phenoxydiphenyl sulphone which, after recrystallization from ethanol had m.p. 112°–113°C. (128 g, 39% yield). A residue, presumably the diphenoxy compound remained in the distillation flask.

4-Fluoro-4'-phenoxydiphenyl sulphone (164 g, 0.5 mol), diphenyl carbonate-4,4'-disulphonyl chloride (103 g, 0.25 mol), nitrobenzene (250 cm³) and ferric chloride (1 g) were stirred at 100°–110°C until evolution of HCl ceased. The total product was stirred with methanol in a laboratory blender until a solid separated out. This was then slurried in methanol (2 l) and 1 mol of aqueous potassium hydroxide added with stirring at room temperature. The resulting solution was filtered, ice was added, and then concentrated hydrochloric acid to effect neutralization. The precipitate was filtered off, recrystallized from acetic acid (decolourizing with charcoal), dissolved in ethanol (decolourizing with charcoal) precipitated into iced water and finally recrystallized again from acetic acid to give XII, (81 g, 33% yield) m.p. 225°–8°C. Found: C, 58.6; H, 3.5; S, 12.4; F, 3.8%. $C_{24}H_{17}O_6S_2F$ requires C, 59.5; H, 3.5; S, 13.2; F, 3.9%. N.m.r. (60 MHz), chemical shifts recorded as δ ppm from tetramethyl silane, were recorded and interpreted thus:

F'—⟨ ⟩—SO₂—⟨ ⟩—O—⟨ ⟩—SO₂—⟨ ⟩—OH

H$_A$ H$_B$ H$_C$ H$_D$ H$_E$ H$_F$ H$_G$ H$_H$
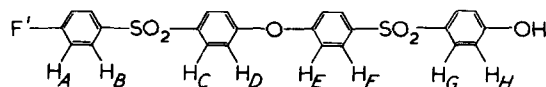
δ (dimethyl sulphoxide) 7.99 (q, 2H$_B$, J_{AB} 8 Hz, $J_{F'B}$ 5 Hz); 7.95 and 7.18 (*ABq*, 2H$_C$, 2H$_D$, J_{CD} 8.5 Hz); 7.91 and 7.18 (*ABq*, 2H$_F$, 2H$_E$, J_{EF} 8.5 Hz); 7.77 and 6.93 (*ABq*, 2H$_G$, 2H$_H$, J_{GH} 9 Hz); 7.34 (t, 2H$_A$, $J_{F'A}$ 8 Hz) ppm.

Classical Syntheses

4-Fluoro-3'-hydroxydiphenyl sulphone. The 4-fluoro-3'-nitro derivative[13] (140 g, 0.5 mol) was heated to reflux with ethanol (2 l) and then stannous chloride (360 g, 2.0 mol) was added in portions, interspersed with portions of concentrated hydrochloric acid (0.65 l, 8 mol in all), so that reflux was maintained. After this addition the mixture was heated to reflux for 1 h more, cooled and made strongly alkaline with potassium hydroxide solution. The precipitate which separated out was filtered off, washed with water and recrystallized from ethanol to give 4-fluoro-3'-aminodiphenyl sulphone, m.p. 105°–107°C.

4-Fluoro-3'-aminodiphenyl sulphone (325 g, 1.3 mol) was dissolved in glacial acetic acid (0.6 l), sulphuric acid (200 g) diluted with water (400 cm³) added and the mixture cooled to 0°C. A solution of sodium nitrite (150 g) in water was added slowly so that the reaction temperature did not exceed 5°C. The solution of diazonium salt was then poured slowly into refluxing 50% sulphuric acid, and the orange crystals which separated on cooling were filtered off. Purification by sublimation under vacuum, followed by decolourizing a methanol solution with active charcoal and recrystallizing the product twice from toluene gave 4-fluoro-3'-hydroxydiphenyl sulphone (165 g, 55% yield) m.p. 150°–151°C. Found: C, 58.4; H, 3.6; F, 7.7%. $C_{12}H_9O_3SF$ requires C, 57.2, H, 3.6; F, 7.6%.

4-Fluoro-2'-hydroxydiphenyl sulphone. 4-Fluoro-2'-nitrodiphenyl sulphide (1513 g, 6.08 mol[14]) was dissolved in glacial acetic acid (6 l) at 70°C, sodium tungstate (6 l) was added and then 30% hydrogen peroxide (1516 cm³) added at a rate such that the stirred reaction mixture boiled under reflux. After stirring overnight the product was poured into iced water (5 l) and the precipitate filtered off, washed with a little methanol and dried under vacuum. The yield of sulphone, m.p. 141°–2°C was 1600 g (94%). Reduction of the sulphone with stannous chloride using the procedure described above gave 4-fluoro-2'-aminodiphenyl sulphone, m.p. 122°–3°C, in 97% yield and conversion of this compound to the diazonium derivative followed by hydrolysis in refluxing dilute sulphuric acid gave an 80% yield of 4-fluoro-2'-hydroxydiphenyl sulphone, m.p. 113°–114°C after vacuum sublimation and recrystallization from a mixture of benzene and light petroleum (b.p. 60°–80°C). Found: C, 57.4; H, 3.9; S, 13.0; F, 7.8%. $C_{12}H_9O_3SF$ requires C, 57.2; H, 3.6; S, 12.7; F, 7.5%.

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