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PENTAFLUOROPHENYLSULFUR(IV) DERIVATIVES

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SUMMARY

A new series of pentafluorophenylsulfur(IV) derivatives $C_6F_5S(O)X$, where X is OLi, OH, Cl, F, OCH_3, $N(CH_3)_2$ and C_6F_5, and pentafluorophenylsulfur trifluoride have been prepared. Pentafluorophenylsulfur(II) derivatives are inert to oxidation to sulfur(IV) by normal procedures, but reaction of pentafluorophenyllithium with sulfur dioxide, or silver difluoride oxidative fluorination of the disulfide, provided good synthetic approaches. Chemical reactions and physical properties of these compounds are compared to those of the hydrocarbon sulfur(IV) analogs and of divalent and hexavalent sulfur derivatives, particularly with regard to spectral properties.

INTRODUCTION

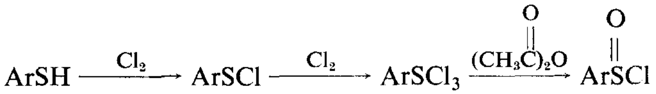
The pentafluorophenyl ring is a unique substituent that imparts improved stability and increased solubility to many organometallics[1,2]. It has an inductive electronegative effect that is much stronger than phenyl but weaker than trifluoromethyl (σ_I = C_6F_5 0.25, CF_3 0.39, C_6H_5 0.08)[3]. However, the π system of the pentafluorophenyl ring is probably severely distorted relative to phenyl and many of the unusual properties of pentafluorophenyl compounds could result from a combination of the inductive effects of five fluorines coupled with strong fluorine–π interactions. Although a wide variety of perfluoroalkylsulfur derivatives have been reported[4], the known sulfur derivatives of pentafluorobenzene are primarily divalent, based on pentafluorothiophenol[5]. Pentafluorobenzenesulfonyl chloride and several sulfones are prepared by oxidation of the divalent sulfur compounds. Only recently pentafluorobenzenesulfenyl chloride and the series of pentafluorobenzenesulfenic derivatives have been reported[6].

We undertook a program to prepare the unknown pentafluorophenylsulfur(IV) derivatives as well as selected unknown pentafluorophenylsulfur(II) and (VI) derivatives so that a complete series of pentafluorophenylsulfur derivatives could be examined to compare effects of pentafluorophenyl substitution on chemical and spectral properties.

RESULTS

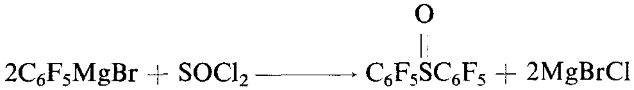
Synthesis

Initial efforts to prepare pentafluorobenzenesulfinyl chloride by adaptation of literature procedures proved unsuccessful. The chlorination of pentafluorobenzenesulfenyl chloride did not appear to give the pentafluorophenylsulfur trichloride intermediate nor pentafluorobenzenesulfinyl chloride under conditions where phenylsulfur trichloride is formed and converted to benzenesulfinyl chloride[7].



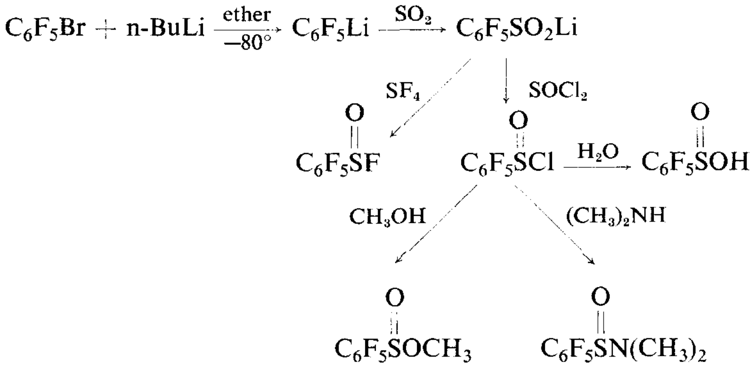
$$\mathrm{ArSH} \xrightarrow{\mathrm{Cl_2}} \mathrm{ArSCl} \xrightarrow{\mathrm{Cl_2}} \mathrm{ArSCl_3} \xrightarrow{(\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_2\mathrm{O}} \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{Cl}$$

Pentafluorophenylmagnesium bromide reacted with excess thionyl chloride to yield primarily bis-(pentafluorophenyl) sulfoxide



$$2\mathrm{C_6F_5MgBr} + \mathrm{SOCl_2} \longrightarrow \mathrm{C_6F_5}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{C_6F_5} + 2\mathrm{MgBrCl}$$

By reaction of the Grignard reagent with sulfur dioxide followed by thionyl chloride, a low yield of pentafluorobenzenesulfinyl chloride was isolated as a distillable liquid. The preferred procedure is to treat pentafluorophenyllithium with sulfur dioxide in ether solution and filter off the insoluble lithium pentafluorobenzenesulfinate in almost quantitative yield; this salt is readily converted by thionyl chloride in high yield to pentafluorobenzenesulfinyl chloride.



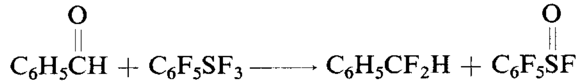
Lithium pentafluorobenzenesulfinate also serves as an intermediate to pentafluorobenzenesulfinyl fluoride by reaction with sulfur tetrafluoride. The sulfinyl chloride was converted to the stable crystalline *N,N*-dimethylpentafluorobenzenesulfinamide and the distillable liquid methyl pentafluorobenzenesulfinate. The sulfinyl chloride readily hydrolyzes (even in moist air) to pentafluorobenzenesulfinic acid, which can be isolated as a crystalline monohydrate. This acid appears to be more stable than perfluoro-2-propanesulfinic acid[8] and at least as stable as trifluoromethanesulfinic acid[9], but decomposes on heating to 120° to yield some pentafluorobenzene. Lithium pentafluorobenzenesulfinate in the dry state decomposes (slowly turns dark) above 280°. In water it slowly decomposes at 80° to yield pentafluorobenzene, similar to decomposition of boiling basic solutions of trifluoromethanesulfinic acid to yield trifluoromethane[9].

The oxidative fluorination of bis-(pentafluorophenyl) disulfide with silver difluoride in trichlorotrifluoroethane solvent was a much more sluggish reaction than in the corresponding phenyl system[10]. The reaction required extended refluxing which caused considerable attack on glass and high contamination of the pentafluorophenylsulfur trifluoride with pentafluorobenzenesulfinyl fluoride. However, pentafluorophenylsulfur trifluoride of high purity was obtained in good yield by reaction in a Hastelloy pressure vessel at 50° under autogenous pressure.

Pentafluorophenylsulfur trifluoride has served as a reagent to prepare the first sulfurane with four carbon bonds to sulfur[11].

$$3C_6F_5Li + C_6F_5SF_3 \xrightarrow{-78^\circ} (C_6F_5)_4S \xrightarrow{0^\circ} C_6F_5\text{–}C_6F_5 + C_6F_5SC_6F_5$$

This sulfurane can be detected and isolated up to 0°. In contrast, phenylsulfur trifluoride reacts with phenyl-lithium to give biphenyl and diphenyl sulfide at −80°[10]. Pentafluorophenylsulfur trifluoride, like phenylsulfur trifluoride, reacted with benzaldehyde to give α,α-difluorotoluene[12].



$$C_6H_5\overset{\overset{O}{\|}}{C}H + C_6F_5SF_3 \longrightarrow C_6H_5CF_2H + C_6F_5\overset{\overset{O}{\|}}{S}F$$

However, pentafluorophenylsulfur trifluoride appears less reactive (lower yield of product and some recovered benzaldehyde under similar conditions) but could have special applications for carbonyl fluorinations such as better control with highly reactive carbonyls or selectivity with polyfunctional reactants.

Physical and spectral properties

The pentafluorobenzenesulfinyl derivatives have slightly lower boiling points than the corresponding phenyl compounds but markedly better thermal stability than the phenyl or alkyl series. Benzenesulfinyl chloride decomposes on standing at room temperature and *p*-toluenesulfinyl chloride has been stated to be unsafe to distil[13]. However, pentafluorobenzenesulfinyl chloride gave no indication of decomposition during distillation or on standing at room temperature for several days. As indicated above, pentafluorobenzene-sulfinic acid, -sulfinamide and -sulfinate methyl ester all appear more stable than the corresponding benzenesulfinic derivatives. Another advantage of pentafluorophenyl substitution is the increased solubility of these sulfur derivatives, especially the sulfonic acid derivatives, in organic solvents.

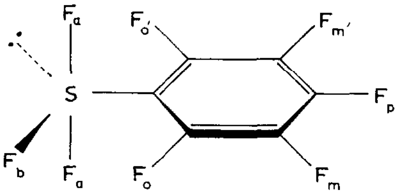
The ultraviolet spectra of the pentafluorophenylsulfur(IV) derivatives are tabulated in Table 1 along with the physical and analytical data. No significant changes in the position or intensity of absorption of the arylsulfur derivatives are apparent as a result of the substitution of the phenyl ring by five fluorines.

The IR spectra of pentafluorophenyl derivatives have been noted to have a characteristic absorption at 760–900 cm^{-1} assigned to X–C_6F_5 bond vibrations, in addition to the strong C–F and ring vibration peaks[14]. In the pentafluorophenylsulfur series a strong peak is usually present at 760–860 cm^{-1} for the sulfur(II) derivatives, but appears weaker or shifted for the sulfur(IV) and sulfur(VI) derivatives.

The ^{19}F NMR chemical shifts of the pentafluorophenylsulfur derivatives can be compared from Table 2. The trends in *meta* and *para* shifts correspond approximately to those expected from the electronic effects of the substituents[15] but only qualitative comparisons are possible[16,17].

The *ortho* shifts for the sulfinyl derivatives are all considerably upfield and for the sulfur(II) series are all markedly downfield, both relative to the sulfur(VI) series. The different geometry and molecular size of the sulfur in the different oxidation states as well as the ligands attached to sulfur would be expected to produce unpredictable variations in chemical shifts by direct through-space and steric interactions.

Pentafluorophenylsulfur trifluoride, pentafluorobenzenesulfinyl fluoride and -sulfonyl fluoride all have the additional S–F resonances which show coupling between the S–F and the *ortho* fluorines. In addition, the sulfinyl fluoride has a long-range six-bond coupling with the *para* fluorine. Pentafluorophenylsulfur trifluoride has an unusual low-temperature spectrum with two sets of *ortho* and *meta* fluorines which is attributed to a trigonal-bipyramid structure (I) with the



(I)

pentafluorophenyl ring in the basal plane and restricted from rotating. The single basal fluorine couples strongly with one *ortho* fluorine and weakly with the other *ortho* fluorine, but the two apical fluorines couple equally with both *ortho* fluorines[18].

TABLE 1

NEW PENTAFLUOROPHENYLSULFUR DERIVATIVES—PHYSICAL AND ANALYTICAL PROPERTIES

Compound	B.p. (pressure)	n_D^{25} or m.p.(°C)	UV		Formula	Carbon		Hydrogen		Fluorine		Sulfur		Other		
			$\lambda_{max.}$	ε		c	f	c	f	c	f	c	f		c	f
$C_6F_5SO_2H{\bullet}H_2O$	—	62–63°	244 265	1 275 1 125	$C_6HF_5O_2S$	28.8	28.7	1.2	1.5	38.0	36.9	12.8	12.8			
$C_6F_5SO_2Li$	—	decomp. 280–300°	258	8 460	$C_6F_5LiO_2S$	30.3	30.3	—	—	39.9	39.5	13.5	13.4	Li	2.9	2.8
C_6F_5SOCl	65° (2.5 mmHg)	1.5042	245 278	4 020 2 680	C_6ClF_5OS	28.8	29.1	—	—	37.9	40.5	12.8	13.0	Cl	14.1	14.7
C_6F_5SOF	43° (3.5 mmHg)	—	213 268	8 360 2 020	C_6F_6SO	30.8	30.9	—	—	48.7	48.7	13.7	13.7			
$C_6F_5SO(OCH_3)$	78° (2.3 mmHg)	1.4670	259	2 800	$C_7H_3F_5O_2S$	34.2	34.3	1.23	1.30	38.6		13.0	13.2			
$C_6F_5SON(CH_3)_2$	100° (2 mmHg)	36–37	220 265(sh) 330(sh)	>950 2 640 80	$C_8H_6F_5NOS$	37.1	37.1	2.32	2.45	36.7	36.2	12.4	11.9	N	5.40	4.20
$(C_6F_5)_2SO$	—	77–78	227 270	15 000	$C_{12}F_{10}OS$	37.7	37.4	—	—	49.7	50.6	8.40	8.76			
$C_6F_5SF_3$	37.5° (4.0 mmHg)	—	—	—	C_6F_8S	28.1	28.5	—	—	59.3	59.9					
$C_6F_5SN(CH_3)_2$	54° (2 mmHg)	1.4732	271 295	2 300 1 130	$C_8H_6F_5NS$	39.5	39.8	2.48	2.76	39.1	39.1	13.2	13.0	N	5.76	5.94
$C_6F_5SO_2F$	103.5° (52 mmHg)	1.4296	210 273	8 200 2 000	$C_6F_6O_2S$	28.8	28.6	—	—	45.6	45.9	12.8	12.8			
$C_6F_5SO_2N(CH_3)_2$	—	117–118°	222 268	5 970 1 330	$C_8H_6F_5NO_2S$	34.9	35.0	2.19	2.27	34.5	34.5	11.6	12.1	N	5.09	4.90

c = calculated, f = found

TABLE 2

^{19}F CHEMICAL SHIFTS[a] OF PENTAFLUOROPHENYLSULFUR DERIVATIVES

X of C_6F_5X	$-\varphi_o$	$-\varphi_m$	$-\varphi_p$
-F	163.0	163.0	163.0
-H	138.7	162.6	154.3
-SH[b]	137.5	162.3	159.1
$-SK \bullet H_2O$[c]	140.5	170.3	177.5
-SNa[c]	140.7	172.5	179.5
-SCl	128.3	160.6	146.1
$-SF_3$[d]	137.2	160.7	145.8
$-SCH_3$[e]	135.8	164.4	157.2
$-S-C_6F_5$[f]	132.4	160.5	150.5
$-S-S-C_6F_5$[f]	131.8	160.1	148.5
$-SN(CH_3)_2$	130.0	161.6	150.7
-SOCl	140.9	159.2	145.7
-SOF[g]	142.8	158.8	146.4
$-SO-C_6F_5$	140.2	159.6	147.6
$-SON(CH_3)_2$	142.1	161.5	151.0
$-SO_2H \bullet H_2O$	139.5	161.1	155.5
$-SO(OCH_3)$	142.9	160.5	148.6
$-SO_2Cl$[h]	134.5	157.6	140.3
$-SO_2F$[i]	133.2	158.1	141.6
$-SO_2C_6F_5$[j]	135.4	158.4	142.3
$-SO_2N(CH_3)_2$	136.2	160.1	147.9

[a] Chemical shifts are ppm upfield from $CFCl_3$. According to newly adopted standards these values are all negative. Unless indicated otherwise all are determined at 10% concentration in $CFCl_3$ as solvent and internal reference at 25°. The coupling patterns are as normally observed (ref. 17).

[b] Benzene solvent, ref. 16.

[c] Acetone solvent. W. BECK, K. H. STETTER, S. TADROS AND K. E. SCHWARZHAUS, *Chem. Ber.*, *100* (1967) 3944.

[d] S–F at +71.9 and –75.3 ppm at –80°.

[e] Chloroform solvent. F. J. HOPTON, A. J. REST, O. T. ROSEVEAR AND F. G. A. STONE, *J. Chem. Soc. (A)* (1966) 1326.

[f] Carbon tetrachloride solvent. M. L. N. REDDY AND A. G. MASSEY, unpublished results (see ref. 1).

[g] S–F at +6.08 ppm.

[h] Chloroform solvent. M. I. BRUCE, *J. Chem. Soc. (A)* (1968) 1459.

[i] S–F at +73.8 ppm.

[j] Acetone solvent. R. D. CHAMBERS, J. A. CUNNINGHAM AND D. J. SPRING, *J. Chem. Soc. (C)* (1968) 1560.

Conclusions

The new class of pentafluorophenylsulfur(IV) derivatives and several new pentafluorophenylsulfur(II) and (VI) derivatives have provided a sufficiently complete series of pentafluorophenylsulfur derivatives for a meaningful comparison of properties. The perfluoro-substitution of the aromatic ring clearly improves stability and solubility relative to the hydrocarbon analogs. In addition, this series of derivatives is a starting point for further synthetic exploration such as preparation of the sulfuranes with four carbon–sulfur bonds[11] and free-radical studies *. The NMR results indicate that the pentafluorophenylsulfur series could provide fundamental information about structure, bonding and geometry of sulfur in various oxidation states.

EXPERIMENTAL

Pentafluorothiophenol was obtained from Pierce Chemical Company and bromopentafluorobenzene from Imperial Smelting Company, England. Silver difluoride was obtained from Ozark–Mahoning. Pentafluorobenzenesulfenyl chloride[6] was prepared by reaction of pentafluorothiophenol with chlorine in carbon tetrachloride containing a catalytic amount of iodine. Pentafluorobenzenesulfonyl chloride[19] was prepared from reaction of pentafluorothiophenol with chlorine and hydrogen peroxide in acetic acid. Bis-(pentafluorophenyl) disulfide[20] was prepared by bromine oxidation of pentafluorothiophenol in acetic acid.

The physical and analytical data on all new compounds are given in Table 1.

Lithium pentafluorobenzenesulfinate (nc)

Bromopentafluorobenzene (123.5 g, 0.50 mole) in ether (250 ml) was added drop-wise to *n*-butyllithium in hexane (320 ml, 0.50 mole) cooled to —70°. The temperature rose to —64° during the addition and was held below —64° for 1.5 h. Dry sulfur dioxide gas was then bubbled into the reaction at —70° for 3 h; a white precipitate formed after 1 h. The lithium pentafluorobenzenesulfinate was suction filtered and air dried, yield, as a fine white powder, 112 g (94%). Attempted purification from hydroxylic solvents, such as ethanol, was unsuccessful and led to decomposition. The crude lithium pentafluorobenzenesulfinate was analytically pure and used directly for synthesis.

Lithium pentafluorobenzenesulfinate decomposes (sinters and darkens) slowly above 280°. When a solution of 5.0 g (0.021 mole) in 100 ml of water was heated at 80° for 2 h, gas was evolved and an oil separated. The oil was identified as pentafluorobenzene (2.73 g, 77%) by comparison to an authentic sample.

Pentafluorobenzenesulfinyl chloride (nc)

Lithium pentafluorobenzenesulfinate (98 g, 0.41 mole) was added to 400 ml of thionyl chloride at room temperature. A mild exothermic reaction occurred on addition. The solid was filtered off and the filtrate vacuum-distilled at 62° (2.2 mmHg) to give 86 g (83% yield) of pentafluorobenzenesulfinyl chloride.

Pentafluorobenzenesulfinyl fluoride (nc)

Lithium pentafluorobenzenesulfinate (23.8 g, 0.10 mole) and 75 ml of trichlorofluoromethane were charged into a 240 ml Hastelloy steel pressure vessel. The

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* The radical reactions of the pentafluorophenylsulfur halides are under study by Dr. J. F. Harris in this laboratory.

pressure vessel was cooled to —80°, charged with 10.8 g (0.10 mole) of sulfur tetrafluoride and heated at 50° for 2 h. It was cooled to room temperature and vented and the solution removed and distilled. Pentafluorobenzenesulfinyl fluoride, b.p. 41–43° (3.5 mmHg) was obtained in a yield of 4.7 g (20%).

Methyl pentafluorobenzenesulfinate (nc)

Pentafluorobenzenesulfinyl chloride (20.9 g, 0.084 mole) was added to methanol (300 ml) and cooled to 0°. The ice bath was removed and the reaction was stirred at room temperature for 2 h. Excess methanol was evaporated and the residue was distilled. Methyl pentafluorobenzenesulfinate, b.p. 78° (2.3 mmHg) was obtained in a yield of 15.5 g (75.0%).

N,N-*Dimethylpentafluorobenzenesulfinamide (nc)*

Pentafluorobenzenesulfinyl chloride (7.68 g, 0.03 mole) in ether (30 ml) was added to a —30° solution of dimethylamine (6.0 ml, 0.09 mole) in ether (30 ml) over 15 min. A white precipitate (dimethylammonium chloride) formed immediately. After the addition was complete, the mixture was allowed to warm to room temperature and stirred for 30 min. The salt was filtered off, the ether was evaporated and the product was distilled at 95–110° (2 mmHg) to give the sulfinamide in a yield of 3.53 g (45.5%). The distillate crystallized and was purified by recrystallization from petroleum ether to give white crystals m.p. 36–37°.

Pentafluorobenzenesulfinic acid (nc)

Water (1.0 ml) was added to pentafluorobenzenesulfinyl chloride (9.53 g, 0.038 mole) in ether (225 ml) cooled to 0°. The reaction was stirred for 1.5 h at room temperature. Magnesium sulfate was added and the solution was filtered and evaporated. An oil (4.6 g, 48%) partially crystallized. Pure pentafluorobenzenesulfinic acid monohydrate was separated by trituration with petroleum ether. Pentafluorobenzenesulfinic acid hydrate melts at 62–63° and decomposes at 120° to give pentafluorobenzene and a black residue.

Bis-(pentafluorophenyl) sulfoxide (nc)

Bromopentafluorobenzene (12.35 g, 0.05 mole) was added to magnesium turnings (1.22 g) in ether (50 ml) and was maintained at a gentle reflux during the addition. The Grignard was added drop-wise to a —20° solution of thionyl chloride (4 ml) and ether (12 ml). The reaction mixture was warmed to room temperature after the addition was complete, filtered and washed well with water. The ether solution was dried and distilled to give bis-(pentafluorophenyl) sulfoxide in a yield of 7.1 g (74% yield), recrystallized from cyclohexane m.p. 77–8°. The experiment was repeated with excess thionyl chloride at —50° and the results were the same.

Pentafluorophenylsulfur trifluoride (nc)

A flame-dried 100 ml pressure vessel was charged in a dry box with 25.9 g (0.065 mole) of bis-(pentafluorophenyl) disulfide, 40 g (0.28 mole) of powdered silver difluoride and 50 ml of 1,1,2-trichlorotrifluoroethane. The pressure vessel was heated with rocking for 5 h at 50°, cooled and the contents transferred in a dry box for distillation. The pentafluorophenylsulfur trifluoride, distilled in a spinning-band column, b.p. 41–42° (5.2 mmHg), was obtained in a yield of 18.8 g (56%). In attempted preparations using the literature procedure[10], the reaction of silver difluoride and disulfide was found to require refluxing in the solvent and resulted in major attack on the glass reaction pot so that the product was nearly half pentafluorobenzenesulfinyl fluoride.

N,N-*Dimethylpentafluorobenzenesulfenamide (nc)*

The procedure described for the sulfinimide was employed using pentafluorobenzenesulfenyl chloride and dimethylamine. The product was distilled, b.p. 54° (2 mmHg), and obtained in 51% yield.

N,N-*Dimethylpentafluorobenzenesulfonamide (nc)*

Pentafluorobenzenesulfonyl chloride (8.0 g, 0.03 mole), and triethylamine (5.0 ml, 0.036 mole) were stirred in 30 ml ether while 2.0 g (0.03 mole) dimethylamine was added slowly. After the addition was complete, the reaction was allowed to warm to room temperature. The salt was removed and extracted with ether. The combined ether extract and filtrate were evaporated to a gummy oil which was recrystallized from cyclohexane. The yield of pure *N,N*-dimethylpentafluorobenzene sulfonamide was 3.5 g (42.5%).

Pentafluorobenzenesulfonyl fluoride (nc)

Pentafluorobenzenesulfonyl chloride (6.75 g, 0.025 mole) in 25 ml of acetonitrile with about 5 g of sodium fluoride powder was stirred and refluxed for 8 h. The product was distilled collecting 4.9 g (78%) pentafluorosulfonyl fluoride b.p. 103.5° (52 mmHg).

Reaction of pentafluorophenylsulfur trifluoride with benzaldehyde

Benzaldehyde (2.87 g, 0.027 mole) was added to 6.94 (0.027 mole) of pentafluorophenylsulfur trifluoride. A slight temperature rise was noted on mixing. The reaction mixture was gradually heated to 100° and the product vacuum-distilled collecting 1.9 g (52%) of α,α-difluorotoluene b.p. 52–55° (44 mmHg) and 5.89 g of liquid b.p. 67–68 (18 mmHg) that was a mixture of pentafluorobenzenesulfinyl fluoride and some recovered benzaldehyde.

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