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Arylsulfur Pentafluorides[1]

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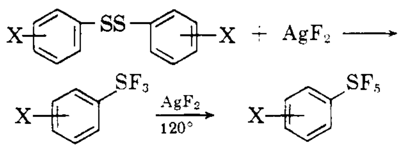
The first synthesis of phenylsulfur pentafluoride has been accomplished by reaction of the corresponding disulfide with silver difluoride. Phenylsulfur trifluoride is formed as an intermediate and may also be isolated and employed as the starting material. By protecting the aromatic ring with a deactivating nitro group, nitrophenylsulfur pentafluorides are obtained in yields of 15 to 30%. The stability of arylsulfur pentafluorides is comparable to that of benzotrifluorides. Because of the inertness of the sulfur pentafluoride group to strong oxidizing and reducing conditions as well as strong acids and bases, it has been possible to prepare a series of arylsulfur pentafluorides with substituents such as NH_2, NHCOR, halogens, OH, N_3, CO_2H, NNR. The sulfur pentafluoride group, like the trifluoromethyl group, is electron-withdrawing and orients substitution by an electrophilic reagent to the *meta* position.

A general synthesis of arylsulfur trifluorides was described previously.[2] Until recently, the only organic derivatives of sulfur hexafluoride were those with perfluoroalkyl groups prepared in moderate to poor yields by methods employing elemental fluorine or electrolytic fluorination in liquid hydrogen fluoride.[3] In the last year the addition of sulfur chloropentafluoride to olefins has been reported to provide a general route to alkylsulfur pentafluorides.[4] However, arylsulfur pentafluorides cannot be prepared from sulfur chloropentafluoride[5] and were not obtained in other fluorination studies.[6]

Results and Discussion

Synthesis.—The first synthesis of arylsulfur pentafluorides has been accomplished by the reaction of aryl disulfides or arylsulfur trifluorides with silver difluoride at 120° (equation 1).

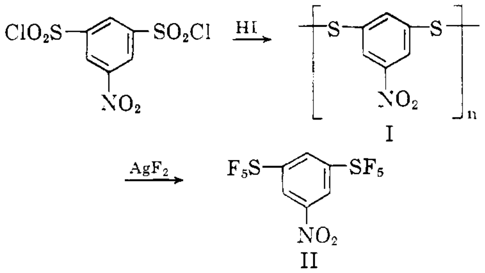


(1)

Initially it was found that phenylsulfur trifluoride reacted with silver difluoride at 120 to 130° in a "Teflon" (polytetrafluoroethylene) reactor and phenylsulfur pentafluoride was distilled from the reaction mixture under reduced pressure in a yield of 5 to 14%. Impurities resulting from addition or substitution of fluorine on the phenyl ring were removed in part by base washing and distillation. However, in order to obtain an analytical sample, it was necessary to remove the last 1 or 2% of impurity by preparative gas chromatography.

A modified procedure for preparation of phenylsulfur pentafluoride was addition of phenyl disulfide to five molar equivalents of silver difluoride suspended in 1,1,2-trichloro-1,2,2-trifluoroethane ("Freon" 113), in a copper reactor. After the exothermic reaction subsided, the "Freon" was distilled, the reaction mixture heated to 120° and the phenylsulfur pentafluoride was distilled under reduced pressure. This modified procedure was found particularly useful for the reaction of bis-(*m*- and *p*-nitrophenyl)-disulfides with silver difluoride. In these cases the initial reaction of the disulfides with the AgF_2 in the "Freon" solvent required several hours refluxing (the disulfides have only low solubility in the "Freon") and the *m*- and *p*-nitrophenylsulfur pentafluorides were extracted from the reaction mixture with a solvent such as chloroform. The products, again purified by distillation, were obtained in yields of 15 and 30%, respectively, for the *para* and *meta* isomers. Because of the deactivating effect of the nitro group, no significant amount of impurities resulted from fluorination of the aromatic nucleus.

The above procedure has also been employed for the preparation of an aromatic compound substituted with two sulfur pentafluoride groups. In this case the polymeric disulfide I was prepared from reaction of 5-nitrobenzene-1,3-disulfonyl chloride with hydriodic acid. The fluorination of disulfide I, first in the "Freon" solvent, then at 120° gave 5-nitrophenyl-1,3-bis-(sulfur pentafluoride) II in low yield. Bis-(*o*-nitrophenyl)-disulfide could be fluorinated to the trifluoride in the "Freon" solvent with silver difluoride,[2] but decomposition occurred when the reaction temperature reached about 100–120°. Intramolecular oxidation-reduction between the SF_3 and NO_2 group apparently occurs more readily than fluorination.[7] On the basis of the present work it is expected that any aromatic disulfide with substituents inert to silver difluoride, particularly deactivating substituents



I

II

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(1) This work was reported in a preliminary form by W. A. Sheppard, *J. Am. Chem. Soc.*, **82**, 4751 (1960), and at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

(2) W. A. Sheppard, *ibid.*, **84**, 3058 (1962).

(3) (a) For a recent review of compounds containing sulfur–fluorine bonds see H. L. Roberts, *Quart. Rev.*, **15**, 30 (1961). (b) R. D. Dresdner and J. A. Young, *J. Am. Chem. Soc.*, **81**, 574 (1959), reported that electrolytic fluorination of $(CH_3S)_2$ gave a low yield of CH_3SF_5 and $CH_3SF_4CH_2F$, isolated as a mixture.

(4) J. R. Case, N. H. Ray and H. L. Roberts, *J. Chem. Soc.*, 2066 and 2070 (1961).

(5) See ref. 3a, pp. 41 and 43.

(6) H. J. Emeleus and H. G. Heal, *J. Chem. Soc.*, 1126 (1946).

(7) D. L. Chamberlain, D. Peters and N. Kharasch, *J. Org. Chem.*, **23**, 381 (1958), suggested that an intramolecular oxidation-reduction reaction occurred in the reaction of *o*-nitrobenzenesulfenyl chloride and HF to give bis-(2,2'-fluorosulfonyl)-azobenzene.

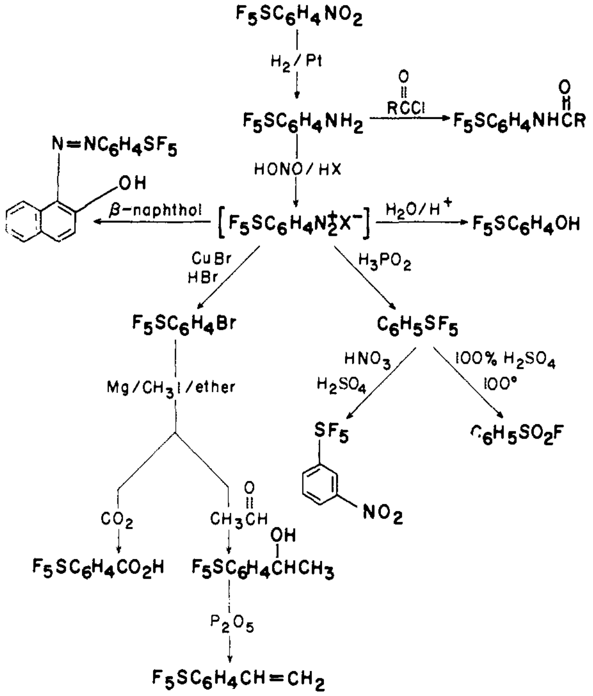
such as Cl, F, SO_2F and COF, readily can be converted to the arylsulfur pentafluorides.

Physical and Chemical Properties.—Phenylsulfur pentafluoride is a colorless liquid, b.p. 149° and density 1.49 g./ml. It has a pleasant aromatic odor, unlike that usually observed with aromatic sulfur compounds, and it is soluble in common organic solvents, including pentane. The compound has chemical and thermal stability comparable to benzotrifluoride. It is recovered unchanged from refluxing in a solution of sodium hydroxide in aqueous ethanol, and no fluoride could be detected by analysis of the solution. It is inert to concentrated sulfuric acid at moderate temperatures but is hydrolyzed to benzenesulfonyl fluoride by heating at 100° in 100% sulfuric acid. (Benzotrifluoride is hydrolyzed at 95° under the same conditions.) The thermal stability of phenylsulfur pentafluoride was demonstrated by showing that only a small amount of degradation occurs on heating a sample at 400° for several hours in a sealed glass tube.

Phenylsulfur pentafluoride was nitrated with nitric acid in concentrated sulfuric at 40° to give *m*-nitrophenylsulfur pentafluoride in over 80% yield. This indicates that the sulfur pentafluoride group, like trifluoromethyl, is electron withdrawing and *meta*-directing to electrophilic aromatic substitution.

As a further demonstration of the stability of the sulfur pentafluoride group, *m*- and *p*-nitrophenylsulfur pentafluoride are catalytically hydrogenated to the corresponding aminophenylsulfur pentafluorides in over 90% yield. The amino derivatives are stable, white, crystalline solids and react in the manner typical of anilines; thus they can be acylated or diazotized. The diazonium salts may be coupled (for example to β-naphthol), hydrolyzed to phenols, converted to halides by the Sandmeyer reaction or reduced. Reduction provides the best route for preparation of large samples of pure phenylsulfur pentafluoride. The bromophenylsulfur pentafluorides are converted by the entrainment method to the Grignard reagents which in turn have been carbonated to the benzoic acids. Representative reactions are summarized in the flow chart and additional reactions leading to other new arylsulfur pentafluorides[8] are described in the Experimental section. In all of these conversions the sulfur pentafluoride group is inert and yields correspond to those usually reported in analogous literature procedures.

Spectral Properties.—The ultraviolet spectra (λ_{max} and ϵ values) of all the arylsulfur pentafluorides prepared in this work are given in Table I. As expected, the SF_5 group shows no unusual effect on the spectra of the aromatic compounds.



Flow Chart of Representative Reactions of Arylsulfur Pentafluorides

Recently the infrared spectra of some derivatives of sulfur hexafluoride were reported[9] and compared to published spectra of other sulfur–fluorine compounds. It was proposed that strong absorption bands between 580 and 610 cm.$^{-1}$ and very strong bands between 860 and 910 cm.$^{-1}$ are diagnostic for the sulfur pentafluoride group.

The infrared spectra of all the arylsulfur pentafluorides have been examined, and it is apparent that the SF_5 group produces very strong absorption (often the most intense in the spectra) in the 820 to 880 cm.$^{-1}$ region[10] (tabulated in Table I). Unfortunately, many of the substituted aromatic compounds have strong absorption due to C–H deformation in the same region and such absorption is not readily distinguished from that caused by S–F vibrations. Phenylsulfur pentafluoride in the form of pure liquid has very strong broad absorption centered at 833 cm.$^{-1}$; in dilute carbon tetrachloride solution this intense absorption appears as a doublet at 855 and 843 cm.$^{-1}$. Small shifts result from the *meta*- and *para*-substituents, but qualitative correlations are not practical because of the assignment problem with the extraneous absorptions. It should be noted, however, that the region of absorption diagnostic for the SF_5 group should be extended to include a lower limit of approximately 820 cm.$^{-1}$.

A detailed analysis of the F^{19} n.m.r. spectra of arylsulfur pentafluorides in addition to data on the structure and electron-withdrawing properties of the sulfur pentafluoride group is presented in subsequent papers.[11] A point of particular interest is the size of the SF_5 group relative to the aromatic nucleus. From an examination of scale models, it is apparent that steric interactions would occur between the fluorines and an ortho-substit-

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(8) The physical and analytical data for all arylsulfur pentafluorides are given in Table I. Because of space limitations, certain additional examples have not been included.

(9) L. H. Cross, G. Cushing and H. L. Roberts, *Spectrochim. Acta*, **17**, 344 (1961); see also ref. 4 and L. H. Cross, H. L. Roberts, P. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 945 (1960).

(10) No attempt was made to study the absorption in the 600 cm.$^{-1}$ region. The remainder of the spectrum from 650 to 5000 cm.$^{-1}$ was typical of the aromatic group.

(11) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3072 (1962); D. R. Eaton and W. A. Sheppard, publication in preparation.

TABLE I
ARYLSULFUR PENTAFLUORIDES

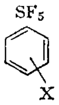
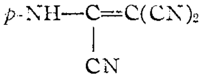
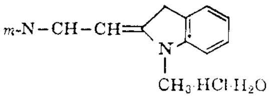
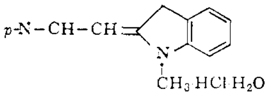
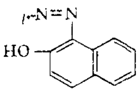
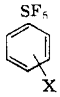
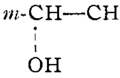
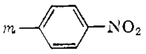
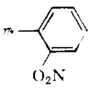
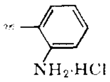
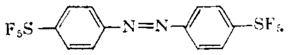
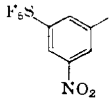
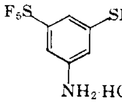
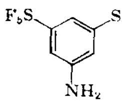
Substituent X of 	M.p. (°C.) and/or $n^{25}\text{D}$	B.p. (°C.)	Ultraviolet[a] $\lambda_{\max}$ (mμ)	$\epsilon_{\max}$	Infrared absorption[b] (cm.$^{-1}$)
H	∼−10 1.4293	148.6[c] (72.0/48 mm.)	267[d] 261 254 249	630 740 510 290	833
m-NO$_2$	∼0 1.4735	85.5/2.6 mm.	243	8,032	847 833
p-NO$_2$	37.5–38.5 1.4660	76–77/2.0 mm.	242 287	8,720 370	865 (sh) 847 828
m-NH$_2$	37	86.5/3.2 mm.	304 244	2,300	850 (broad) 837
p-NH$_2$	67.5–68.0	...	280 (broad) 247	1,425 14,350	850 to 820
m-NH$_2$·HCl	...	...	304 244	1,940 9,860	876 (mw) 840 822 (sh)
p-NH$_2$·HCl	Decomp. over 160	...	256	14,600	840 820 (ms)
 $m\text{-NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{C}_6\text{H}_5$	166–167	...	262	15,500	878 (m) 868 (m) 848 840 812
 $p\text{-NH}-\underset{\text{CN}}{\underset{\mid}{\text{C}}}=\text{C(CN)}_2$	196–196.5 (decomp.)	...	351 240	17,100 5,830	862 (m) 847 842 (sh) 833 (sh) 822 (mw)
	150–154	...	384.5 418	39,500 47,560	833 (ms) 817 (ms)
	145–149	...	390[f] 305 (broad) 245 421	39,500 4,384 11,850 51,400	855 (sh) 837 813
p-N$_3$	1.4918	57.5/1.0 mm.	255 286 (sh)	15,900 2,480	843 828 (ms) ?
	203–203.5	...	474 420 305, 250 227	18,300 sh Broad, weak 36,200	868 (ms) 853 to 843 822
m-OH	66.5	81.5/3.0 mm.	282 220	2,770 5,540	868 851 840
p-OH	104–105	...	278 271 265 (sh) 230	860 1,100 1,000 10,750	849 837 830 (sh) 820 (sh)

TABLE I (*Continued*)

Formula and mol. wt.	Carbon		Hydrogen		Fluorine		Sulfur		Other	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_6H_5SF_5$ 204.2	35.3	35.9^{e}	2.47	2.78	46.5	46.5	15.7	15.6^{f}	M.W.	166^{h}
		35.5		2.74		46.7				
$C_6H_4NO_2SF_5$ 249.2	28.9	29.7^{e}	1.62	1.83	38.1	38.4	12.9	13.0	N 5.63	5.14
		29.7		1.96		38.5		13.1		5.33
		29.6		1.97						
		29.9^{g}		2.06^{g}		38.4^{g}		12.9^{g}		5.39^{g}
		29.6		1.90		38.4				
$C_6H_4NO_2SF_5$ 249.2	28.9	29.1	1.66	1.85	39.1	38.1	12.9	12.9	N 5.63	5.14
						38.4				5.17
						38.5			M.W.	202^{h}
										306^{i}
$C_6H_6NSF_5$ 219.2	32.9	33.5	2.76	3.10	43.3	44.1	14.6	15.1	N 6.40	6.31
		33.5		3.04		44.2		15.3		6.36
		33.1^{g}		3.17^{g}		44.3^{g}		15.0^{g}		6.62^{g}
									N.E.	221
										222
$C_6H_6NSF_5$ 219.2	32.9	33.7	2.76	2.79	43.4	43.3			N 6.40	6.31
		33.5		2.92						
		33.2							N.E.	221
$C_6H_7NSF_5Cl$ 255.6	28.2	28.5	2.76	3.16	37.2	37.4	12.6	12.9	N 5.48	5.45
									Cl 13.9	14.3
$C_6H_7NSF_5Cl$ 255.6	28.2	28.4	2.76	2.87	37.2	36.9	12.6	12.2	N 5.48	5.42
		28.5^{g}		3.00^{g}		37.2^{g}		12.5^{g}		5.53^{g}
								12.5	Cl 13.9	13.5
								12.4		
$C_{13}H_{10}ONSF_5$ 323.3	48.3	48.5	3.13	3.02	29.4	29.4	..	..	..	..
$C_{11}H_5N_4SF_5$ 320.2	41.3	41.3	1.58	1.65	29.7	30.7			N 17.5	16.7
$C_{19}H_{19}N_2SF_5 \cdot HCl \cdot H_2O$ 375.3	49.9	49.9	4.85	5.00	20.8	20.8			N 6.13	6.07
		50.0		5.92						6.17
$C_{19}H_{19}N_2SF_5 \cdot HCl \cdot H_2O$ 375.3	49.9	50.6	4.85	4.97	20.8	20.7			N 6.13	6.07
		50.5		4.82						6.11
$C_6H_4N_3SF_5$ 245.2	29.4	30.1	1.65	2.15	38.8	38.4	..	..		
						38.4				
$C_{16}H_{11}N_2OSF_5$ 374.4	51.5	51.8	2.96	3.16	25.4	26.3			N 7.48	7.32
		51.8		3.12		24.6				7.47
$C_6H_5OSF_5$ 220.2	32.7	32.8	2.29	2.45	43.1	42.8				
		32.9		2.73						
$C_6H_5OSF_5$ 220.2	32.7	33.0	2.29	2.40	43.1	43.1				

TABLE I (*Continued*)

Substituent X of 	M.p. (°C.) and/or $n^{22}D$	B.p. (°C.)	Ultraviolet[a]		Infrared absorption[b] (cm.$^{-1}$)
			λ_{max} (mμ)	ϵ_{max}	
p-Cl	1.4553	77/17 mm.	272	260	850 to 820
			267	310	
			264	330	
			262	360	
			255 (sh)	260	
			221	13,280	
m-Br	1.4775[h]	82.0/12 mm.	277[i]	820	837 to 843
			271	940	
			264	620	
p-Br	1.4880	77.2/10 mm.	262.5[i]	370	840 to 830
			227	12,200	820
m-CO_2H	153.0–155.2	...	277.5	560	870
			270	700	857
			263	570	835
			222	8,920	818 (mw)
p-CO_2H	191.5–192.5	...	282	1,310	870 (m)
			273	1,560	847 (sh) ?
			223	12,820	843
					833 (sh)
 $m\text{-}\underset{\text{OH}}{\text{CH}}\text{—CH}_3$	1.4621	86/1.4 mm.	272	820	850 to 830
			264	870	
			258	620	
m-CH=CH_2	1.4706	74.5/10.0 mm.	293	600	840
			283	940	
			277	900	
			255 (sh)	8,700	
			247	13,800	
m-C_6H_5	20.5–21.5	112.5–113.5/2.0	248	16,200	850 to 833
	1.532	mm.			
	128.6–129.0	...	290	16,600	870 } (m)
			220 (sh)	14,100	855 }
					844
					826 (mw)
	81.0–81.7	...	290 (sh)	2,050	880 (ms)
			227	16,400	867 (ms)
					843
	...	...	310	1,300	867 (sh)?
			231	9,650	842
	175.2–175.9	...	275 to 270	sh	855 (ms)?
			230	21,700	840 to 830
Bis-Sulfur pentafluoride derivatives					
	163–164	...	453	232	870 (sh)
			313	18,400	848
			253	7,440	813 (ms)
			225	9,640	
	71-72	88/1.6 mm.	237[i]	7,500	877 (ms)
					862 ?
					850
					834
	...	...	319	13,160	...
			251	10,300	
	80.7–81.5	...	321	2,700	878 (m)
			252	12,100	870 (sh)
					853
					837
					812 (w)

[a] The n.m.r. fluorine spectra have been obtained on the majority of compounds in this table, and with minor variation the pattern is the characteristic one described in ref. 11. [b] Only the strong absorptions in the 810 to 900 cm.$^{-1}$ region listed from spectra obtained on pure liquids, or solids in KBr pellet. Many of these absorptions may be assigned to the S–F vibrations, but positive assignment is precluded because of confusion with a strong absorption for hydrogen out-of-the-ring deformation that falls in the region of 800–860 cm.$^{-1}$. The absorption for phenylsulfur pentafluoride becomes a doublet at 855 and 843

TABLE I (*Continued*)

Formula and mol. wt.	Carbon		Hydrogen		Fluorine		Sulfur		Other	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_6H_4ClSF_5$ 238.6	30.2	30.7	1.69	1.91	..	..	..		Cl 14.9	14.8
$C_6H_4BrSF_5$ 283.1	25.5	25.7	1.42	1.68	33.6	33.8	11.3	11.3	Br 28.2	28.0
$C_6H_4BrSF_5$ 283.1	25.5	25.9 25.9	1.42	1.59 1.63	33.6	33.6			Br 28.2	28.3
$C_7H_5O_2SF_5$ 248.2	33.9	34.3 34.2	2.02	2.13 2.21	38.3	38.5			N.E. 248.2	249.8
$C_7H_5O_2SF_5$ 248.2	33.9	34.2	2.02	2.10	38.3	38.6			N.E. 248.2	244.2
$C_8H_9OSF_5$ 248.2	38.7	39.1	3.66	3.81	38.3	37.2				
$C_8H_7SF_5$ 230.2	41.7	41.8	3.07	3.04	41.3	41.1				
$C_{12}H_9SF_5$ 280.3	51.4	51.1	3.24	3.27	33.9	33.4				
$C_{12}H_8NO_2SF_5$ 325.3	44.3	44.7[l] 44.6[m]	2.48	2.58[l] 2.67[m]	29.2	29.3[l] 29.1[m]			N 4.31	3.83[l]
$C_{12}H_8NO_2SF_5$ 325.3	44.3	44.8[l]	2.48	2.60[l]	29.2	28.9[l]			N 4.31	3.92[l]
$C_{12}H_{19}NSF_5 \cdot HCl$ 331.8	43.4	43.4	3.35	3.98						
$C_{19}H_{14}NOSF_5$ 399.4	57.1	57.4	3.54	3.97	23.8	22.8				
$C_{12}H_8N_2S_2F_{10}$ 434.3	33.2	33.2	1.85	2.04	43.8	43.0			N 6.47	6.38
$C_6H_3NO_2S_2F_{10}$ 375.2	19.2	19.2	0.81	0.93	50.6	50.5	17.1	16.7[f]*	N 3.74 M.W.	3.70 460[i]
$C_6H_6NS_2F_{10} \cdot HCl$ 381.7	18.9	19.3	1.59	1.60	49.8	50.4			N 3.67 N.E.	3.09 3.35 456
$C_6H_5NS_2F_{10}$ 345.2	20.9	21.2	1.46	1.48	55.0	55.3			N 4.06 N.E.	4.01 4.04 290.4

cm.$^{-1}$ on dilution in carbon tetrachloride. [c] Density of phenylsulfur pentafluoride 1.4936 g./ml. [d] Ethanol used as solvent unless stated otherwise. [e] It has been observed in compounds containing C, F. and S, that the C analysis is often 0.4 to 0.7% high, although not reproducibly so. [f] Analysis by oxyhydrogen combustion procedure. It was found that the Parr bomb method generally gave low, nonreproducible results on the sulfur pentafluoride derivatives. Any S analysis made by this method is indicated by *f. [g] Second sample. [h] F.p. in benzene. [i] B.p. in benzene. [j] Solvent isoöctane. [l] Prepared by Gomberg reaction. [m] Prepared by nitration of biphenylsulfur pentafluoride. [n] Density 1.82 g./ml.

ent of atomic radius greater than hydrogen or fluorine. Chemical evidence for such interaction is presented by the decomposition that occurred in attempted fluorination of *o*-nitrophenylsulfur trifluoride.

Experimental

Materials.—Silver difluoride (argentic fluoride) was obtained from the Harshaw Chemical Company. Phenylsulfur trifluoride was prepared as described previously.[2] Bis-(*m*-nitrophenyl)-disulfide was prepared by the literature procedure[12] and purchased from Aldrich Chemical Company. 1,1,2-Trichloro-1,2,2-trifluoroethane ("Freon-113") was obtained from Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware. All other reagents described in this work were obtained from chemical supply houses such as Eastman Chemical.

Phenylsulfur Pentafluoride. A. From Phenylsulfur Trifluoride.—Phenylsulfur trifluoride (8.0 g., 0.84 mole) and 18 g. (0.12 mole) of silver difluoride were placed in a 30-ml. pot with condenser, both fabricated from "Teflon" polytetrafluoroethylene resin.[13] The exit of the condenser was connected by copper and "Tygon" tubing to a glass trap cooled in a Dry Ice–acetone bath. The reaction mixture was heated in an oil bath at 115–130° for 1 hr. The pressure in the system was then gradually reduced to 5 mm. and the product distilled into the cold trap. An ether solution of the product was washed with 5% sodium hydroxide solution, dried over magnesium sulfate and distilled. A total of 1.4 g. (14%) of phenylsulfur pentafluoride was collected as a clear, colorless liquid, b.p. 67–79° (40 mm.).[14] The phenylsulfur pentafluoride was contaminated with impurities resulting from the addition and substitution of fluorine on the aromatic ring. A pure sample of phenylsulfur pentafluoride was obtained by use of a preparative-scale gas chromatographic column. The sample was passed through a 1.3 cm. by 1.8-m. column packed with silicone oil and firebrick heated at 130°, using helium carrier gas, and the purified phenylsulfur pentafluoride redistilled, b.p. 148.6°, n^{25}_{D} 1.4293, d^{25}_{25} 1.4936. Phenylsulfur pentafluoride is very soluble in pentane, ether, benzene and other common organic solvents. The analytical data, and ultraviolet and infrared spectra are given in Table I. The F^{19} n.m.r. spectrum had a resonance pattern similar to that assigned to the SF_5 group in CF_3SF_5.[11] A single resonance in the aromatic region was observed for the H^1 spectra.

B. From Phenyl Disulfide.—This reaction was run in a 1-l. copper pot fitted with a "Teflon" cover held in place by "C" clamps. A stainless steel paddle stirrer and "Teflon" bearing, glass addition funnel, and "Teflon" condenser were accommodated through three holes drilled in the cover. Silver difluoride (350 g., 3.4 moles) and 100 ml. of CCl_2FCClF_2 were charged into the dry pot and the apparatus was assembled. A solution of 40 g., (0.18 mole) of phenyl disulfide dissolved in 250 ml. of CCl_2FCClF_2 was added dropwise to the stirred reaction mixture. After the addition was complete and the exothermic reaction had subsided, the reaction mixture was heated in an oil bath at 50–60° and the CCl_2FCClF_2 distilled. The residue was then heated at 120–130° for 2 hr. A Dry Ice trap was connected to the exit of the condenser and the pressure was gradually reduced to 10 mm. The product collected in the Dry Ice trap was worked up as described above. The yield of crude material, b.p. 50–75° (38 mm.) was 6.5 g. (9% yield based on disulfide). This sample contained a much larger amount of impurities as noted above and no improvement in yield was obtained by modification of conditions of reaction time and temperature.

***p*-Nitrophenylsulfur Pentafluoride.**—This reaction was carried out in the copper pot with "Teflon" fittings as described above but with a "Teflon" plug in place of the addition funnel; the apparatus was thoroughly dried and protected from atmospheric moisture with a "Drierite" guard tube. The pot was charged with 46.2 g. (0.15 mole) of bis-(*p*-nitrophenyl)-disulfide, 270 g. (1.8 mole) of silver difluoride, and 200 ml. of CCl_2FCClF_2. The reaction mixture was heated to reflux with stirring for 1 hr. in an oil bath at 50–60°. The CCl_2FCClF_2 was distilled from the reaction mixture and the oil-bath temperature was raised gradually (*Caution*: rapid heating at this point was found to cause an uncontrolled reaction leading to charring) to 120–135° and maintained there for 2 hr. After cooling, the reaction mixture was a pasty yellow solid and was extracted with several 150-ml. portions of carbon tetrachloride followed by two 100-ml. portions of chloroform. The combined extracts were distilled and the resulting residue of yellow oil and orange solid was fractionated through a 45-cm. spinning-band distillation column to give 8.6 g. (11.5%) of *p*-nitrophenylsulfur pentafluoride, b.p. 89.2° (3.8 mm.), n^{25}_{D} 1.4660, as a pale-yellow liquid which on standing crystallized in large prisms, m.p. 37–38°. In a subsequent series of three preparations in which the products were combined, a total of 35.6 g. (16%) of *p*-nitrophenylsulfur pentafluoride was obtained. The analytical and spectral data are given in Table I. The F^{19} n.m.r. spectrum was essentially identical with that of phenylsulfur pentafluoride.

***m*-Nitrophenylsulfur Pentafluoride.**—*m*-Nitrophenylsulfur pentafluoride was prepared from bis-(*m*-nitrophenyl)-disulfide by the method described above. (*Caution*: In the addition of the bis-(*m*-nitrophenyl)-disulfide to the silver difluoride suspension in CCl_2FCClF_2, an exothermic reaction was observed to occur after a short induction period.) In a typical preparation using 42.0 g. (0.136 mole) of the disulfide with 250 g. (1.7 moles) of silver difluoride and 200 ml. of CCl_2FCClF_2, a yield of 21.6 g. (31%) of *m*-nitrophenylsulfur pentafluoride, b.p. 85.5° (2.6 mm.), n^{25}_{D} 1.4735, was obtained. Preparations in the same equipment using double quantities of reagents gave yields of 28–30%.

5-Nitrophenyl-1,3-bis-(sulfur pentafluoride) (II).—From the reduction of 57.3 g. (0.18 mole) of 5-nitrobenzene-1,3-disulfonyl chloride[15] with 260 ml. (approximately 1.8 moles) of 55% hydriodic acid solution,[12] the poly-5-nitrophenyl-1,3-bis-(disulfide) (I) was obtained as a pale-yellow powder, m.p. 177–181°, in a yield of 31.0 g. (92.8%).

Anal. Calcd. for $(C_6H_3O_2NS_2)x$: C, 38.9; H, 1.6; N, 7.56; S, 34.6. Found: C, 38.4; H, 1.6; N, 7.50; S, 34.5.

The fluorination of 60 g. (0.325 mole) of the polydisulfide I with 550 g. (3.8 moles) of silver difluoride in 500 ml. of $CClF_2CFCl_2$ was carried out as described above. The reaction product was extracted with several portions of hot chloroform. From evaporation of the chloroform extracts, there was obtained an orange tar which on extraction with hot benzene left a residue of intractable gum. From evaporation of the benzene extract there was obtained 29 g. of an orange oil that partly crystallized on standing. Although it was found that the product could be extracted into pentane, the best method of purification was distillation. A total of 14.0 g. (11.5%) of 5-nitrophenyl-1,3-bis(sulfur pentafluoride), b.p. 93.5° (2.4 mm.), m.p. 70–72°, was obtained. In other preparations it was found very difficult to control the fluorination reaction and much lower yields of product resulted.

Aminophenylsulfur Pentafluorides.—Platinum oxide, 0.30 g., was added to a solution of 8.3 g. (0.033 mole) of *p*-nitrophenylsulfur pentafluoride and 6.3 ml. of 5.5 *N* hydrogen chloride in ethanol (0.035 mole of hydrogen chloride) in 100 ml. of absolute ethanol, and the mixture was placed in a 500-ml. pressure bottle in a Parr hydrogenation apparatus. The system was flushed and pressured to 40 lb. with hydrogen and shaken. Approximately the calculated 0.10 mole of hydrogen was absorbed in less than 30 minutes. The catalyst was removed by filtration and the ethanol solution was evaporated at room temperature under nitrogen or at reduced pressure. The solid residue was triturated with 100 ml. of ether, suction filtered, and washed with additional ether. The *p*-aminophenylsulfur pentafluoride hydrochloride was obtained in a yield of 8.5 g. (90%) as a fine white powder and was analytically pure. *p*-Aminophenylsulfur pentafluoride as the free base was obtained by adding with stirring 3.0 g. (0.118 mole) of the above hydrochloride in portions to 60 ml. of 10% aqueous sodium carbonate covered with a layer of 25 ml. of ether. The ether layer was separated and the aqueous solution extracted twice with ether. The

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(12) W. A. Sheppard, *Org. Syn.*, **40**, 80 (1960).

(13) Wide-mouth reactors were machined from blocks of "Teflon" and were fitted with a screw cap also machined from "Teflon." For a condenser, a threaded hole was drilled in the cap and a piece of 1.3-cm. i.d. "Teflon" pipe with threaded ends was screwed into the cap. The pipe was surrounded externally with a glass jacket using rubber stoppers for end seals, and the jacket was provided with an inlet and exit at opposite ends for circulation of condenser water.

(14) All boiling points and melting points are uncorrected.

(15) G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, 266 (1929).

combined ether extracts, after drying over anhydrous magnesium sulfate, were distilled to obtain *p*-aminophenyl sulfur pentafluoride as a white, crystalline solid. Further purification was accomplished by recrystallization from pentane at low temperatures to give white needles, m.p. 67.5–68.0°.

m-Aminophenylsulfur pentafluoride was prepared by reduction of *m*-nitrophenylsulfur pentafluoride as described above. The physical and spectral properties and analytical data for these anilines are given in Table I. Both *m*- and *p*-aminophenylsulfur pentafluorides are, by contrast to aniline, stable to air oxidation and do not discolor readily on exposure to air. The hydrochlorides are nonhygroscopic.

From the reduction of 5.56 g. of *p*-nitrophenylsulfur pentafluoride in ethanol *without* hydrogen chloride, employing a microhydrogenation apparatus, 3.94 of the *p*-aminophenylsulfur pentafluoride was separated by extraction with ether–pentane from 0.83 g. of orange-crystals, m.p. 163–164°. This orange solid after recrystallization from carbon tetrachloride was characterized as bis-(*p*,*p*′-pentafluorosulfo)-azobenzene.

5-Aminophenyl-1,3-bis-(sulfur pentafluoride).—5-Nitrophenyl-1,3-bis-(sulfur pentafluoride) (II), 9.7 g. (0.0259 mole) was dissolved in 100 ml. of absolute ethanol containing 5.5 ml. of 5.0 *N* hydrogen chloride in ethanol and 300 mg. of platinum oxide. Reduction was carried out in a Parr hydrogenation apparatus as described above. The resulting solution was filtered and evaporated under nitrogen and the residue triturated with ether. There was obtained 4.03 g. of the amine hydrochloride as white fluffy crystals; 3.44 g. of additional material was obtained by concentration of the ether washings. The free aniline was obtained by treating 4.33 g. of the hydrochloride salt with 100 ml. of 10% sodium carbonate solution. The product, 5-aminophenyl-1,3-bis-sulfur pentafluoride), was obtained by extraction with ether in a yield of 3.50 g. It was purified by recrystallization from hexane and by sublimation to a constant m.p. 80.7–81.5°.

Reactions of Aminophenylsulfur Pentafluoride.—The experimental details are analogous to typical reactions of aniline and its derivatives as described in the literature.[16] The physical and analytical data on the compounds prepared by these reactions are given in Table I.

Carboxyphenylsulfur Pentafluorides.—The Grignard reagents of bromophenylsulfur pentafluorides could not be prepared by reaction with magnesium in ether, and a modification of the entrainment method was found necessary. A mixture of 1.43 g. (0.059 mole) of magnesium turnings in 5 ml. of dry ether was placed in a dry, nitrogen-flushed 100-ml. flask fitted with a magnetic stirrer, addition funnel, reflux condenser with Drierite guard tube and thermometer. A solution of 5.90 g. (0.0208 mole) of *m*-bromophenylsulfur pentafluoride and 2.84 g. (0.020 mole) of methyl iodide in 25 ml. of dry ether was added dropwise to the above mixture. An exothermic reaction started immediately, and the rate of addition of the solution was adjusted to maintain a gentle reflux. The addition required about 20 minutes, and the resulting solution was refluxed for an additional 40 minutes. The reaction was then chilled to −7° in an ice-salt bath and carbonated in the normal manner. The pasty residue obtained from ether extraction after acidification was washed with water and recrystallized from ethanol–water to yield 3.92 g. of the crude *p*-carboxyphenylsulfur pentafluoride, m.p. 140–144°. The product was further purified by recrystallization from hexane and benzene and finally by sublimation at 100–120° (5 mm.). The yield of pure acid, m.p. 153.0–155.2°, was 2.85 g. (55.2%).

By the same preparation and purification procedure as described above, 5.90 g. of *p*-bromophenylsulfur pentafluoride was converted to 1.97 g. (38.0% yield) of *p*-carboxyphenylsulfur pentafluoride, m.p. 191.5–192.5°.

***m*-(1-Hydroxyethyl)-phenylsulfur Pentafluoride.**—The Grignard reagent was prepared as described above from 9.5 g. (0.0333 mole) of *m*-bromophenylsulfur pentafluoride, 4.7 g. (0.0333 mole) of methyl iodide and 1.70 g. (0.070 mole) of magnesium in 40 ml. of dry ether. The Grignard solution was cooled and 4.5 ml. (3.5 g., 0.08 mole) of acetaldehyde in 10 ml. of chilled ether was added gradually by use of a syringe. After the exothermic reaction had subsided, the reaction mixture was hydrolyzed with 10 ml. of 25% aqueous ammonium chloride. The ether solution was decanted and the aqueous residue extracted with ether. The combined ether extracts were dried over magnesium sulfate and distilled. The *m*-(1-hydroxyethyl)-phenylsulfur pentafluoride, b.p. 86° (1.4 mm.), $n^{21}_{\rm D}$ 1.4637, was obtained in a yield of 3.6 g. (43.5%). In an initial preparation in which a much smaller proportion of methyl iodide to bromophenylsulfur pentafluoride was employed, a much lower yield of the desired product was obtained, and considerable bromophenylsulfur pentafluoride was recovered.

***m*-Pentafluorosulfostyrene.**—*m*-(1-Hydroxyethyl)-phenylsulfur pentafluoride, 3.15 g. (0.0127 mole), 0.20 g. of phosphorus pentoxide and 0.05 g. of hydroquinone (inhibitor) were mixed in a pot attached to a 30-cm., semimicro spinning-band still. The pot was heated gradually from 100 to 170° with an oil bath, as the pressure in the system was reduced from 150 to 47 mm. The pentafluorosulfostyrene distilled as formed at 81–94° (approximately 47 mm.) in a yield of 2.15 g. (73.7%). The product was further purified by dissolving in a small amount of ether, drying over anhydrous magnesium sulfate and redistilling (hydroquinone inhibitor added), to yield 1.7 g., b.p. 74.5° (10.0 mm.), $n^{27}_{\rm D}$ 1.4698.

A sample of *m*-pentafluorosulfostyrene was polymerized by heating in benzene solution with benzoyl peroxide initiator.[17] The polymer was pressed into a clear, colorless, brittle film typical of a polystyrene prepared under these conditions.

Reactions of Phenylsulfur Pentafluoride. (a) **Nitration.**—Phenylsulfur pentafluoride, 4.13 g. (0.0202 mole), was mixed with 12 ml. of concentrated sulfuric acid in a 25-ml. flask fitted with magnetic stirrer, addition funnel, reflux condenser and thermometer. Fuming nitric acid, 4 ml., was added dropwise at a rate such that the reaction temperature remained between 35 and 40°. The mixture was heated in an oil bath at 50°, and an additional 3 ml. of fuming nitric acid was added during 2.5 hr. The cooled reaction mixture was poured into 200 ml. of cracked ice and water, and the product separated as a light yellow oil which was extracted into ether. The combined ether extracts were washed with 5% sodium hydroxide and water and then dried over anhydrous magnesium sulfate. The ether solution was distilled through a short, packed column, and the residue fractionated through a 30-cm. semimicro spinning-band column. A total of 4.05 g. (80.6%) of *m*-nitrophenylsulfur pentafluoride, b.p. 83.5° (2.2 mm.), $n^{25}_{\rm D}$ 1.4741, was obtained. The product was characterized as *m*-nitrophenylsulfur pentafluoride by infrared spectra and melting point of 0°. There was no indication of any *p*-isomer.

Verification of this result by vapor phase chromatography was not successful. Separation of a control mixture of *m*- and *p*-nitrophenylsulfur pentafluorides could not be made on a series of chromatographic columns with a packing range suitable for separation of fluorocarbons or aromatic isomer mixtures.

(b) **Hydrolysis. Basic Conditions.**—Phenylsulfur pentafluoride, 0.201 g. (0.001 mole), was mixed with 10.0 ml. of 1.04 *N* aqueous (5%) sodium hydroxide solution in a 25-ml. flask fitted with a magnetic stirrer and reflux condenser. The reaction mixture was heated in a water bath at 94–96° for 4 hr. Aliquots (2.0 ml.) of the solution were removed at the end of 30 minutes, 2 hr., and 4 hr. and titrated for fluoride ion. No fluoride ion (less than 0.0001 g./2 ml. aliquot) was detected; the amount of fluoride ion resulting from 0.5% hydrolysis of phenylsulfur pentafluoride could have been detected by this method.

In a second experiment, 0.201 g. of phenylsulfur pentafluoride was dissolved in 10 ml. of 0.52 *N* sodium hydroxide in 50% aqueous ethanol (homogeneous solution). The solution was refluxed for 4 hr. at 95–96° and aliquots taken as above. Again no fluoride ion could be detected, showing that less than 0.5% hydrolysis of the phenylsulfur pentafluoride occurred.

At the end of each experiment the recovered phenylsulfur pentafluoride was shown by spectral analysis to be unchanged.

(c) **Acidic Conditions.**—Sulfuric acid (98–100%) was prepared by mixing 123 g. of concentrated sulfuric acid with 47 g. of fuming sulfuric acid, containing 20–23% of SO_3.

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[16] These experimental details of reactions of aminophenylsulfur pentafluoride in which the sulfur pentafluoride group plays no part have been prepared as Appendices and deposited as Document Number 7142 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm, payable to Chief, Photoduplication Service, Library of Congress.

[17] We are indebted to Dr. A. L. Barney for this experiment.

Phenylsulfur pentafluoride, 2.05 g. (0.010 mole), was mixed with 2.0 g. of the above sulfuric acid in a 15-ml. flask fitted with a magnetic stirrer and a reflux condenser with a Drierite guard tube. The flask was immersed in an oil bath and the contents stirred while the temperature was raised gradually. No reaction was apparent until the oil bath temperature reached 98°, at which point bubbling was observed in the reaction mixture and HF attack was observed on the upper walls of the glass flask. After 5-10 min. heating at 100-103° the reaction was essentially complete, as indicated by the reaction mixture becoming homogeneous. Heating was continued for an additional 40 minutes at 100–103°, and then the reaction mixture was poured over 25 ml. of ice and water. There was obtained a total of 0.75 g. (40%) of oil, characterized by infrared and n.m.r. fluorine spectra as benzenesulfonyl fluoride. Benzenesulfonyl fluoride is hydrolyzed to benzenesulfonic acid under these conditions, and the 60% unrecovered product probably can be accounted for as benzenesulfonic acid which was not isolated in the work-up procedure.

A control hydrolysis of benzotrifluoride was run under the same conditions as above for comparison purposes. It was observed that the benzotrifluoride was hydrolyzed at 90–95° in less than 5 minutes.[18]

(d) **Pyrolysis.**[19]—Samples (0.10 g.) of phenylsulfur pentafluoride were sealed in evacuated 20 mm. × 15 mm. Pyrex glass tubes constructed with a capillary tip. One of each of these tubes was heated for a 7-hr. period at 400, 450 and 500° in a muffle furnace. The tubes, after cooling, were opened in an evacuated holder and the gaseous products were analyzed in a mass spectrometer. The results are given in Table II.

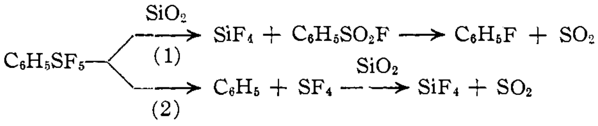
TABLE II

PYROLYSIS OF PHENYLSULFUR PENTAFLUORIDE

	400°	450°[a]
Appearance after heating	Slightly charred deposit. Clear, colorless liquid	Large amount black deposit; clear, colorless liquid
Estimated decomposition[b]	<20%	<40%
Analysis of gaseous products[c]		
SiF_4	49%	29%
SO_2	35%	28%
C_6H_5F	12%	39%
$C_6H_5SF_5$	1%	4%

[a] The tube heated at 500° leaked. It contained very little liquid and was completely black inside; the gaseous product was chiefly air. [b] Estimated from amount of recovered liquid. [c] Liquid product was shown to be chiefly $C_6H_5SF_5$ by spectrometric analysis.

Decomposition could occur at the higher temperature by one of two routes.



$$C_6H_5SF_5 \xrightarrow[(1)]{SiO_2} SiF_4 + C_6H_5SO_2F \longrightarrow C_6H_5F + SO_2$$

$$C_6H_5SF_5 \xrightarrow[(2)]{} C_6H_5 + SF_4 \xrightarrow{SiO_2} SiF_4 + SO_2$$

By analogy to decomposition studies on CF_3SF_5,[20] route 2 is favored. Additional pyrolysis studies of gaseous samples in a nickel cylinder also support this conclusion. In this case decomposition became extensive at 500°, but quantitative studies were precluded by reaction of the sample at high temperatures with traces of moisture in the cylinder walls.

Acknowledgments.—The author is grateful to Drs. T. L. Cairns and B. C. McKusick for helpful discussions and suggestions during the course of this work.

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[18] G. M. LeFave, *J. Am. Chem. Soc.*, **71**, 4148 (1949); E. T. McBee and M. R. Frederick, *ibid.*, **71**, 1490 (1949).

[19] A qualitative study of the stability of derivatives of perfluorobenzene recently was described by L. A. Wall, R. E. Donadio and W. J. Pummer, *ibid.*, **82**, 4846 (1960).

[20] R. E. Dresdner, *ibid.*, **77**, 6633 (1955); **79**, 69 (1957).

[CONTRIBUTION NO. 730 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

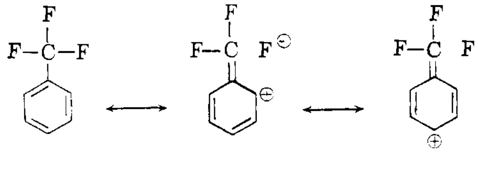
The Electrical Effect of the Sulfur Pentafluoride Group[1]

BY WILLIAM A. SHEPPARD

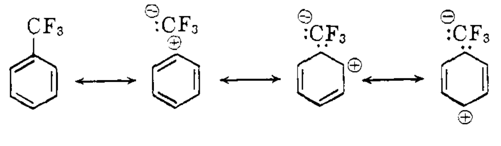
RECEIVED JANUARY 16, 1962

The sulfur pentafluoride group, a new stable substituent on an aromatic ring, has been shown to be strongly electron-withdrawing with measure σ-values, *meta* and *para*, of +0.61 and +0.68 to +0.86, respectively. By ionization constant and dipole moment measurements the electron attracting influence has been shown to be enhanced in the *para* position by a small, but significant, amount of resonance interaction. This resonance effect is discussed relative to a similar effect observed with the trifluoromethyl group and relative to d-orbital participation by sulfur.

The electron-withdrawing power of the trifluoromethyl group on an aromatic ring has been evaluated[2] from dipole moment and σ-parameter data. The strong, inductive electron-withdrawal effect was shown to be enhanced to a significant extent by resonance interaction, and resonance contribution of the following type was suggested



Alternatively, the preferential relay of the electron attracting influence of the trifluoromethyl group to the *o*- and *p*-position may be explained by an induction of a positive charge at C-1 of the aromatic



ring and distribution by resonance over the *o*- and *p*-positions (represented schematically by the resonance structures shown).

Recently, arylsulfur pentafluorides were synthesized for the first time.[3] The sulfur pentafluoride group, like the trifluoromethyl group, was shown to have a strong *meta*-orienting influence in electro-

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[1] This work was presented in part at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

[2] J. D. Roberts, R. L. Webb and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

[3] W. A. Sheppard, *ibid.*, **82**, 4751 (1960) and **84**, 3064 (1962).