and V and the 3-substituted 2-pyridones (VI and VIII) also were shown not to form when neat 1-(1-methylallyl)-2-pyridone (VII) is heated under rearrangement conditions.

**Attempted Isomerization of 2-Crotoxypyridine (IV) to 2-(1-Methylalloxy)pyridine (V).**—Neat IV was heated in sealed tubes at 245°. Samples were withdrawn at 0.5-hr. intervals for 5 hr. and examined for the presence of the isomerized ether (V) by gas chromatography.[18] The column temperature was maintained at 100° for 8 min. before programming began.

No peak due to V was observed in any of the samples. It was determined that no more than 0.5% of V could be present at any time during the rearrangement.

# Aryl Fluoroalkyl Sulfides. I. Preparation by Reaction of Grignard Reagents with Trifluoromethanesulfenyl Chloride[1]

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The reaction of arylmagnesium halides with trifluoromethanesulfenyl chloride provides a new and convenient synthesis of aryl trifluoromethyl sulfides. The scope and mechanism of this reaction is discussed, and the chemical and physical properties of aryl fluoroalkyl sulfides are described.

Aryl trifluoromethyl sulfides have been synthesized by reaction of antimony trifluoride with aryl trichloromethyl sulfides which were in turn prepared by photo-

$$\mathrm{ArSCH_3} \xrightarrow[h\nu]{\mathrm{Cl_2}} \mathrm{ArSCCl_3} \xrightarrow{\mathrm{SbF_3}} \mathrm{ArSCF_3}$$

initiated chlorination of aryl methyl sulfides.[2] This method is only of moderate utility since the aromatic substituents are limited to inert groups such as nitro or halogens, and the aryl methyl sulfides are not readily available.

Phenyl tetrafluoroethyl sulfide has been prepared by base-catalyzed addition of thiophenol to tetrafluoroethylene.[3] However, this reaction has not been ex-

$$\mathrm{C_6H_5SH + CF_2{=}CF_2 \xrightarrow{base} C_6H_5SCF_2CF_2H}$$

tended to substituted thiophenols, and the properties of the tetrafluoroethylthio group have not been studied.

The aryl trifluoromethyl sulfides have been oxidized to the corresponding sulfones by chromic anhydride in sulfuric acid,[2,4] but otherwise the trifluoromethylthio group appears to be inert to normal chemical transformations of the aromatic ring such as reduction of nitro groups,[2] nitration (*ortho–para* orientation),[5] diazotization of amino groups, and hydrolysis of nitriles.[2] Potential dyes[2a,6] and pharmaceutical chemicals[7] containing the $SCF_3$ and $SO_2CF_3$ groups have been reported.

## Results and Discussion

**Synthesis.**—The reaction of arylsulfenyl chlorides with Grignard reagents has been reported as a method for preparation of aryl sulfides.[8] This reaction has now been extended to provide a new direct method for preparation of aryl trifluoromethyl sulfides by reaction of aryl Grignard reagents with trifluoromethanesulfenyl chloride (see Table I).[9]

$$\mathrm{ArMgX + CF_3SCl \longrightarrow ArSCF_3\ (+\ ArCl + ArX)}$$

The sulfide is obtained in a yield of about 50% by bubbling $CF_3SCl$ into a solution of the Grignard reagent at 0°. In addition, aryl chloride and aryl halide are formed as by-products (5 to 15%) from the Grignard reagent (if X is not Cl). In a search for optimum conditions, it was found that, if $CF_3SCl$ was added to a solution of phenylmagnesium bromide chilled to $-40°$ or if an inverse addition procedure was used (maintaining the reaction mixture at $-60°$ to $-80°$), the yield of phenyl trifluoromethyl sulfide decreased but that of bromobenzene increased proportionately. The purification of the product by distillation ($C_6H_5Cl$, b.p. 132°; $C_6H_5SCF_3$, b.p. 142°; $C_6H_5Br$, b.p. 155°) was simplified by use of arylmagnesium chloride,[10] and yields of products were comparable to yield from reaction of the bromide. Purification also was simplified when arylmagnesium iodide was used, but the yield of aryl trifluoromethyl sulfide was significantly lower.

In order to rationalize the results, consideration was given to the mechanism of the reaction. Although mechanism studies have not been reported on the reaction of arylsulfenyl chlorides with Grignard reagents, a mechanism has been proposed for the reaction of Grignard reagents with alkyl halides.[11] The mechanism suggested is a $S_N2$ or a "push–pull" type which involves

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(1) This work was presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961.

(2) (a) French Patent 820,796 (1937); J. Dickey, U. S. Patent 2,436,100 (1948); British Patents 503,920 (1939) and 479,774 (1938); (b) L. M. Yagupolsky and A. I. Kiprianov, *J. Gen. Chem. USSR*, **22**, 2273 (1952); (c) L. M. Yagupolsky and M. S. Marenets, *ibid.*, **24**, 885 (1954).

(3) D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **82**, 5166 (1960).

(4) L. M. Yagupolsky and B. E. Gruz, *J. Gen. Chem. USSR*, **31**, 1219 (1961).

(5) L. M. Yagupolsky and M. S. Marenets, *ibid.*, **26**, 99 (1956).

(6) L. M. Yagupolsky and M. S. Marenets, *ibid.*, **25**, 1725 (1955).

(7) (a) E. A. Nodiff, S. Lipschutz, P. N. Craig, and M. Gordon, *J. Org. Chem.*, **25**, 60 (1960); (b) French Patent 1,245,552 (1960).

(8) H. Lecher, *Ber.*, **58**, 409 (1925); G. E. Hilbert and T. B. Johnson, *J. Am. Chem. Soc.*, **51**, 1526 (1929); G. Sanna, *Gazz. chim. ital.*, **72**, 305 (1942).

(9) Trifluoromethanesulfenyl chloride was originally reported by R. N. Haszeldine and J. M. Kidd [*J. Chem. Soc.*, 3219 (1953)], who prepared it by reaction of $CF_3SSCF_3$ or $(CF_3S)_2Hg$ with $Cl_2$. A convenient synthesis of large quantities of $CF_3SCl$ is the reaction of $CCl_3SCl$ with NaF in tetramethylene sulfone [C. W. Tullock, U. S. Patent 2,884,453 (1959); and C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960)].

(10) Arylmagnesium chlorides are readily prepared in tetrahydrofuran as solvent from aryl chloride and magnesium with isopropyl alcohol or aluminum isopropoxide as initiator [E. T. Blues and D. Bryce-Smith, *Chem. Ind.* (London), 1533 (1960)].

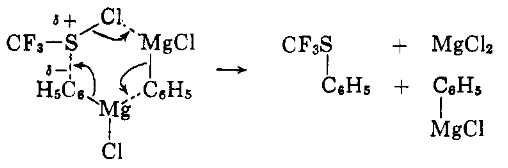
(11) (a) For a general discussion, see M. S. Kharasch and O. Reinmuth "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 1048; (b) C. G. Swain, *J. Am. Chem. Soc.*, **70**, 1119 (1948).

TABLE I

PREPARATION OF ARYL TRIFLUOROMETHYL SULFIDES, $ArMgX + CF_3SY \rightarrow ArSCF_3$

| ArX, g. (mole) for Grignard reagent[a] | Solvent (ml.) and reaction temperature, °C.[b] | $CF_3SCl$, g. (mole) | Products | Yield,[c] % |
|---|---|---|---|---|
| $C_6H_5Br$ 78.5 (0.50) | Ether (500), 0–20 | 70 (0.50) | $C_6H_5SCF_3$[d] | 52 |
| | | | $C_6H_5Cl$ | 11 |
| | | | $C_6H_5Br$ | 6 |
| $C_6H_5Br$[e] 39.2 (0.25) | Ether (250), −40 to −30 | 35 (0.25) | $C_6H_5SCF_3$ | 40 |
| | | | $C_6H_5Cl$ | 3 |
| | | | $C_6H_5Br$ | 24 |
| $C_6H_5Br$[e] 39.2 (0.25) | Ether (250 ml) | 40 (0.28) | $C_6H_5SCF_3$ | 31 |
| | Inverse addition to $CF_3SCl$ in | | $C_6H_5Cl$ | 4 |
| | 150 ml. of ether at −80° | | $C_6H_5Br$ | 43 |
| $C_6H_5Cl$ 22.5 (0.20) | Tetrahydrofuran (150), −10–0 | 30 (0.21) | $C_6H_5SCF_3$ | 54 |
| | | | $C_6H_5Cl$ | 9 |
| $C_6H_5I$ 51.0 (0.20) | Ether (150), −10–0 | 41 (0.29) | $C_6H_5SCF_3$ | 23 |
| | | | $C_6H_5Cl$ | 3 |
| | | | $C_6H_5I$ | 12 |
| *m*-$ClC_6H_4CH_3$ 50.4 (0.40) | Tetrahydrofuran (200), 0–10 | 55 (0.40) | m-$CH_3C_6H_4SCF_3$ | 32 |
| | | | m-$CH_3C_6H_4Cl$ | 3 |
| *p*-$ClC_6H_4CH_3$ 50.4 (0.40) | Tetrahydrofuran (200), 0–10 | 55 (0.40) | p-$CH_3C_6H_4SCF_3$ | 34 |
| | | | p-$CH_3C_6H_4Cl$ | 7 |
| $C_6H_5Cl$ 7.85 (0.07) | Tetrahydrofuran (40), 0–10 | $CF_3SBr$ | $C_6H_5SCF_3$ | 8 |
| | | 11 (0.061) in 20 ml. of | $C_6H_5Br$ | 3 |
| | | tetrahydrofuran | $C_6H_5Cl$ | Trace |

[a] Grignard reagent prepared in normal manner (see "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 550 and ref. 10) using a slight molar excess of magnesium. [b] Unless indicated otherwise, $CF_3SCl$ was bubbled slowly into a solution of Grignard reagent at reaction temperature indicated. [c] Yields determined on total crude product (distilled) by vapor phase chromatographic analysis. [d] B.p. 141–142°, $n^{25}D$ 1.4633, lit.[2c] b.p. 141–142°. [e] Grignard reagent from same preparation.



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a transition state such as **1** (not necessarily a cyclic intermediate).

A similar mechanism is suggested for the sulfenyl halide reaction; like the carbon in alkyl halides, the sulfur of $CF_3SCl$ is slightly more positive in character than the chlorine, and attack by the carbanion species is directed chiefly to sulfur. However, the difference in electron density between Cl and S is sufficiently small that some attack occurs on the chlorine to displace $CF_3S^-$. At low temperatures or under inverse addition conditions employing arylmagnesium bromide, the reaction is sufficiently slow so that $CF_3SBr$ can form through exchange of $CF_3SCl$ with magnesium bromide or aryl magnesium bromide.[12] Bromine is more electronegative and polarizable (the strong electron-withdrawing power of the $CF_3$ group enhances this electronegativity) than chlorine; thus the results described here are explained by competing $Br^-$ or $CF_3S^-$ displacement. Evidence in support of this hypothesis was obtained by treating $CF_3SBr$, prepared by a literature procedure,[13] with phenylmagnesium chloride. Although the over-all yield of isolable products was lowered, the yield of phenyl trifluoromethyl sulfide relative to bromobenzene decreased compared to that of sulfide to bromo- or chlorobenzenes in the $CF_3SCl$ reactions. A similar result has been reported for the reaction of Grignard reagents with cyanogen halides; cyanogen chloride gives benzonitrile but cyanogen bromide gives chiefly bromobenzene.[14] Another example of the different reaction course resulting from differences in electronegativity of halogen has been reported by Kohrich.[15] The reaction of *o*-lithiophenyl phenyl sulfone with benzenesulfonyl fluoride gave *o*-phenylsulfonylphenyl phenyl sulfone, whereas, with benzenesulfonyl chloride, *o*-chlorophenyl phenyl sulfone was the only product.

This synthesis was extended to reaction of *m*- and *p*-tolyl Grignard reagents with $CF_3SCl$ and may be general for any Grignard reagent with a perfluoroalkylsulfenyl chloride. Phenyllithium with $CF_3SCl$ gave a very low yield of product, and mainly tar was formed. The reaction of $CF_3SSCF_3$ with a Grignard reagent would have the advantage of eliminating the aryl halide by-products, but again tar was the principal product.

**Properties.**—The physical and chemical properties of aryl trifluoromethyl sulfides (Table II) have been compared to those of aryl tetrafluoroethyl sulfides and aryl perfluoroalkyl ethers. These sulfides also have been employed in measurements of the electronic effect of fluorine substitution and in study of mechanisms of transmission of inductive and resonance effects.[16]

As generally recognized, the replacement of aliphatic hydrogen by fluorine causes a decrease in boiling point ($C_6H_5SCF_3$, b.p. 142°; $C_6H_5SCH_2CF_2H$, 180° (approx.); and $C_6H_5SCH_3$, 190°). The ultraviolet and infrared

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(12) Sulfenyl halides undergo exchange reactions with metallic salts, for example, KCN and KSCN. However, no reference to studies on exchange with salts of bromides has been found: see (a) N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, **39**, 298 (1946); (b) A. Schoberl and A. Wagner in Houben-Weyl "Methoden der Organischen Chemi Schwefel-, Selen-, Tellur-Verbingdungen, Vol. IX, E. Muller, Ed., Georg Thieme, Stuttgart, 1955, Chapter on sulfenic derivatives.

(13) Difluorobromomethanesulfenyl bromide, obtained from addition of bromine to thiocarbonyl fluoride, was treated with antimony trifluoride [N. N. Yarovenko and A. S. Vasilena, *J. Gen. Chem. USSR*, **29**, 3749 and 3754 (1959)].

(14) Ref. 11a, p. 787.

(15) G. Kohrich, *Ber.*, **92**, 2981 (1959).

(16) (a) W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 1314 (1963); (b) D. R. Eaton and W. A. Sheppard, *ibid.*, **85**, 1310 (1963).

TABLE II.—ARYL FLUOROALKYL SULFIDES. PHYSICAL AND ANALYTICAL DATA

| Compound | B.p. (mm.), °C. | M.p., °C., or $n^{25}D$ | Method of preparation (% yield)[a] | Formula | Analyses,[b] % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Carbon[c] | | Hydrogen | | Fluorine | | Sulfur | | Other | |
| | | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $H_3CC_6H_4SCF_3$, *meta* | 163–164 | 1.4683 | A | $C_8H_7F_3S$ | 50.0 | 50.1 | 3.68 | 3.52 | 29.7 | 29.8 | 16.7 | 17.1 | | |
| *para* | 167–168 | 1.4700 | A | $C_8H_7F_3S$ | 50.0 | 50.6 | 3.68 | 4.03 | 29.7 | 29.2 | 16.7 | 16.3 | | |
| $HO_2CC_6H_4SCF_3$, *meta*[d] | | 75.4–75.9 | C (59) | $C_8H_5F_3O_2S$ | 43.3 | 43.0 | 2.27 | 2.44 | 25.7 | 25.1 | 14.4 | 14.0 | Neut. equiv. 222 | 221<br>221 |
| *para*[e] | | 161–162.4 | C (93) | $C_8H_5F_3O_2S$ | 43.3 | 43.4 | 2.27 | 2.41 | 25.7 | 25.5<br>25.7 | 14.4 | 14.0<br>13.9 | Neut. equiv. 222 | 221<br>222 |
| *m*-$HOC_6H_4SCF_3$ | 91 (11) | 65.4–66.4 | *f* (37) | $C_7H_5F_3OS$ | | | | | 29.4 | 29.8 | 16.5 | 16.7 | | |
| *m*-$O_2NC_6H_4SCF_2CF_2H$ | 80 (0.50) | 1.5060 | B (64) | $C_8H_5F_4NO_2S$ | | | | | 27.8 | 29.1 | 12.6 | 12.6 | N 5.6 | 5.5<br>5.7 |
| $H_2NC_6H_4SCF_2CF_2H$, *meta* | 80 (1.0) | 1.5148 | E (100) | $C_8H_7F_4NS$ | | | | | 33.8 | 33.5 | 14.2 | 13.7 | N 6.2 | 6.6 |
| *para* | 76 (0.50) | 1.5219 | B (78) | $C_6H_7F_4NS$ | | | | | 33.8 | 33.9 | 14.2 | 14.0 | N 6.2 | 6.3 |
| $H_3CC_6H_4SCF_2CF_2H$, *meta* | 95–97 (23–24) | 1.4706 | B (63) | $C_9H_8F_4S$ | | | | | 33.9 | 33.3 | 14.3 | 14.0 | | |
| *para* | 79 (8.5) | 1.4715 | B (59) | $C_9H_8F_4S$ | 48.2 | 48.9 | 3.60 | 3.69 | 33.9 | 33.5 | 14.3 | 14.3 | | |
| $HO_2CC_6H_4SCF_2CF_2H$, *meta* | | 74.6–75.2 | C (40) | $C_9H_6F_4O_2S$ | 42.6 | 43.2 | 2.38 | 2.57 | 29.9 | 29.6 | 12.6 | 12.3 | Neut. equiv. 254 | 252<br>257 |
| *para* | | 171.2–172.4 | C (52) | $C_9H_6F_4O_2S$ | 42.6 | 42.4 | 2.38 | 2.48 | 29.9 | 29.8 | 12.6 | 13.0 | Neut. equiv. 254 | 254<br>256 |

[a] Letter refers to procedure given in Experimental section. Yield only given for compounds prepared by methods other than reported in Table I. [b] All compounds were characterized also by infrared, ultraviolet, and $H^1$ and $F^{19}$ n.m.r. spectra. [c] For compounds containing fluorine and sulfur, carbon analyses are often 0.4 to 0.7% high but not reproducibly so. [d] Lit.[4] m.p. 75–76°. [e] Lit.[2c] m.p. 160–161°. [f] Prepared by diazotization of corresponding aniline followed by hydrolysis (method given by R. H. F. Manske, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 404).

spectra of these derivatives show no unexpected characteristics. The $F^{19}$ n.m.r. spectra have been reported previously.[16b]

The inert character of $SCF_3$ when attached to the aromatic nucleus was indicated in earlier reports.[2,4,7] The $SCF_2CF_2H$ group has been found to be similarly inert, and a series of chemical transformations have been carried out on the aromatic nucleus of the aryl perfluoroalkyl sulfides to prepare a series of anilines, benzoic acids, and phenols for p$K_a$ and $F^{19}$ chemical shift studies. For example, tolyl fluoroalkyl sulfides were oxidized to the corresponding benzoic acids by light-catalyzed bromination to benzal bromide followed by hydrolysis–oxidation with concentrated nitric acid. The thermal stability of the aryl fluoroalkyl sulfides is poorer than that of the corresponding ethers.[17] The sulfides decompose extensively at approximately 500° in a sealed stainless steel tube, whereas the ethers are stable to nearly 600°.

Nitration of phenyl trifluoromethyl sulfide was repeated,[5] and the product composition determined by $F^{19}$ n.m.r. and infrared spectral methods. Gas chromatographic analysis for isomers composition was not a satisfactory method. In agreement with the literature report (where only a chemical analysis method was employed), the product was found to be a mixture of *para* (chiefly) and *ortho* isomers. No *meta* isomer was detected, but nitrophenyl trifluoromethyl sulfones and sulfoxides were by-products arising from oxidation by the nitric acid.[2a] Catalytic hydrogenation of the nitro derivatives was found to be a suitable method for preparation of the anilines.

## Experimental

**Materials.**—The aryl halides and mercaptans were obtained from chemical supply houses. The trifluoromethanesulfenyl chloride, b.p. −2–0°, was prepared from trichloromethanesulfenyl chloride and sodium fluoride in tetramethylene sulfone by the method of Tullock.[8] Bis(trifluoromethyl) disulfide is a by-product in this preparation. Trifluoromethanesulfenyl bromide, b.p. 34–35°, was prepared by the method of Yarovenko and Vasilena[13] by reaction of $CF_2BrSBr$ with a mixture of antimony trifluoride and pentachloride; $CF_2BrSBr$ was prepared by addition of bromine to thiocarbonyl difluoride. *m*-Nitrophenylthiophenol was prepared by dextrose–base reduction of nitrophenyl disulfide.[18] Samples of *m*- and *p*-nitrophenyl trifluoromethyl sulfides were prepared by the literature procedure.[2] Sodium hydride, as a 57% dispersion in mineral oil, was obtained from Metal Hydrides, Inc., Beverly, Mass.

**A. Reaction of Grignard Reagents with $CF_3SCl$.**—The following procedure is typical. A solution of 50.4 g. (0.40 mole) of *p*-chlorotoluene in 200 ml. of anhydrous tetrahydrofuran was mixed with 11.0 g. (0.46 g.-atom) of magnesium turnings and 2.0 g. of aluminum isopropoxide in a 500-ml., three-necked flask under nitrogen.[10] The stirred mixture was heated at reflux overnight until the magnesium had reacted. The solution was cooled to −10° in an ice–acetone bath, and 55 g. (0.40 mole) of $CF_3SCl$ was bubbled slowly into the solution at a rate such that the reaction temperature was maintained at 0 to 5°. The exothermic reaction ceased after approximately 50 g. of $CF_3SCl$ had been added. The solution was allowed to warm to room temperature over several hours, then cooled to 0°, and 500 ml. of 0.25 *N* sulfuric acid added in portions. The reaction mixture was poured into 500 ml. of water, and the product was extracted with two 100-ml. portions of pentane. The combined pentane extracts were washed with water, 10% sodium carbonate solution, and dried over anhydrous $MgSO_4$. The pentane was distilled through a 45-cm. glass helices-packed column, and the crude product distilled through a 45-cm. spinning-band column. A

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(17) W. A. Sheppard, *J. Org. Chem.*, **29**, 1 (1964).

(18) G. M. Bennet and W. A. Berry, *J. Chem. Soc.*, 1669 (1927).

fraction of 29.7 g., b.p. 70–100° (chiefly 95–100°) (90 mm.), was collected. The product yield was determined by gas chromatographic analysis of this sample; pure (95–99%) *p*-tolyl trifluoromethyl sulfide was obtained by careful fractionation through a 45-cm. spinning-band column or a glass helices-packed column.

B. **Addition of Thiophenols to Tetrafluoroethylene.**—The procedure described previously[3] was employed with the following modifications.[19] The thiophenol (0.25–0.50 mole) was dissolved in 150 ml. of dimethoxyethane (glyme), and 10–20 molar % of 53% sodium hydride dispersion in mineral oil was added. When the reaction was complete, the solution was diluted with 150 ml. of dimethylformamide and transferred to the reactor. The tetrafluoroethylene reaction was carried out as previously described,[3] and the product worked up in the normal manner.

C. **Oxidation to Benzoic Acids.**—A solution of 9.60 g. (0.05 mole) of *p*-tolyl trifluoromethyl sulfide and 16.0 g. (0.10 mole) of bromine in 100 ml. of carbon tetrachloride was radiated under reflux overnight with a General Electric sun lamp. At the end of this time, the bromine color had disappeared, and considerable HBr had evolved. The carbon tetrachloride was evaporated at room temperature under a nitrogen stream, and 50 ml. of concentrated nitric acid was added. The mixture was stirred vigorously overnight; bromine gradually evolved, and finally the product separated from the aqueous phase as a solid. The mixture was poured into several hundred milliliters of ice–water, and the solid product was separated by suction filtration and washed thoroughly with water. The yield of crude *p*-(trifluoromethylthio)benzoic acid, m.p. 157–158.5°, was 10.3 g. The product was purified to constant m.p. 161.0–162.4° by recrystallizations from approximately 125 ml. of 60% hexane–40% benzene, followed by sublimation at approximately 100° (5 mm.).

D. **Nitration.**—A solution of 5.0 g. (0.028 mole) of phenyl trifluoromethyl sulfide and 15 g. of concentrated sulfuric acid was cooled to 0°, and 3.2 g. (0.035 mole) of nitric acid (70%) was added dropwise while keeping the reaction temperature at 0°. After addition was completed, the reaction mixture was stirred for 40 min. at 0° and then poured into 200 ml. of ice-water. The oil was extracted in methylene chloride and after drying, the extracts were distilled through a 30-cm. spinning-band column. A total of 4.13 g. of pale yellow liquid, b.p. 90–91° (5.0 mm.), $n^{26}$D 1.5125–1.5165, was identified by infrared and $F^{19}$ n.m.r. analysis as chiefly *p*-nitrophenyl trifluoromethyl sulfide containing 20–30% of a second component with spectral properties characteristic for an *ortho* isomer. No *meta* isomer was detected. Gas chromatographic analysis on a column of 20% Dow Corning high vacuum grease on 60–80-mesh Celite also indicated 20% of a second component, but complete separation was not accomplished on a selection of columns usually suitable for fluorocarbons or aromatic isomer mixtures. A control reference mixture of *meta* and *para* isomers could not be separated under any of the conditions employed. A higher boiling fraction [93–105° (1.5 mm.), $n^{26}$D 1.5515] was shown by spectral analysis (comparison with an authentic sample) to contain some nitrophenyl trifluoromethyl sulfone.

E. **Reduction.**—Chemical reduction of nitrophenyl trifluoromethyl sulfide with stannic chloride has been reported in the literature.[2] In this work, catalytic hydrogenation, as described by the following procedure, was found to be more convenient. A solution of 19.7 g. (0.077 mole) of *m*-nitrophenyl tetrafluoroethyl ether in 150 ml. of absolute ethanol containing 0.08 mole of hydrogen chloride was hydrogenated at approximately 3 atm. of pressure in a Parr apparatus using 0.30 g. of platinum oxide as catalyst. The theoretical amount of hydrogen was absorbed in a few minutes. The catalyst was removed by filtration, and the alcohol solution evaporated under nitrogen. The residual solid was triturated with 100 ml. of ether and filtered. The *m*-(tetrafluoroethylthio)aniline hydrochloride was obtained as white platelets in an approximately quantitative yield of 21 g. The free aniline was obtained by adding the hydrochloride to an excess of a stirred 10% solution of sodium carbonate layered with ether. The aniline obtained from the dried ether extract distilled at 80° (1.0 mm.).

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[19] We wish to thank Dr. D. C. England of this laboratory for suggesting these modifications.

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# Aryl Fluoroalkyl Sulfides. II. Preparation by Condensation of Trifluoromethanesulfenyl Chloride with Aromatic Systems

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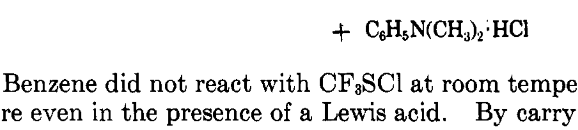
The condensation of trifluoromethanesulfenyl chloride with aromatic compounds provides a convenient new synthesis of aryl trifluoromethyl sulfides. Activated aromatic derivatives, such as phenols or dimethylaniline, react at room temperature without a catalyst to give high yields of the corresponding *p*-substituted aryl trifluoromethyl sulfide. Benzene, toluene, and halobenzenes require higher temperatures and Lewis acid catalysts, such as hydrogen fluoride or boron trifluoride.

In the previous paper,[1] the literature on aryl fluoroalkyl sulfides was reviewed, and the reaction of Grignard reagents with $CF_3SCl$ was described as a new synthetic route to aryl trifluoromethyl sulfides. The condensation of alkyl- or arylsulfenyl chlorides with aromatic compounds has been reported as a method for preparation of aryl sulfides.[2] As an extension of this reaction, we wish to report the convenient preparation of aryl trifluoromethyl sulfides by substitution of aromatic derivatives with $CF_3SCl$. The method is particularly advantageous for aromatic systems with electron-donating substituents.

Introduction of gaseous $CF_3SCl$ into dimethylaniline in ether or phenol in chloroform–pyridine at room temperature gave the corresponding aryl trifluoromethyl sulfide in yields of 58 to 75%. As normally observed in electrophilic, aromatic-type substitutions in aromatic rings highly activated by groups such as $N(CH_3)_2$ or OH, substitution was almost exclusively in the *para* position.



Benzene did not react with $CF_3SCl$ at room temperature even in the presence of a Lewis acid. By carrying out the reaction in a stainless steel autoclave at 100° in the presence of boron trifluoride, phenyl trifluoromethyl sulfide was obtained in a yield of 57%. Similar conditions were needed for reaction with toluene. The over-

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