TABLE III

N.M.R. ANALYSIS OF Na_2S–P_2S_5 GLASSES DISSOLVED IN 10% SODIUM SULFIDE SOLUTION[a]

Na_2S/ P_2S_5	Immediately at 0°	Same solution after 3 hr. at 25°
0	$0.4X + 0.6A$	$0.3PO_2S_2^{=} + 0.7PO_3S^{=}$
0.7	$0.6Y + 0.4A$	$0.5Y + 0.5PO_3S^{=}$
1.0	Y	$0.7Y + 0.3PO_3S^{=}$
1.5	Y	$0.7Y + 0.3PO_3S^{=}$
2.0	Y	$0.2C + 0.6PO_2S_2^{=} + 0.2PO_3S^{=}$
2.5	$0.3Y + 0.7A$	$0.1B + 0.5C + 0.2A + 0.1PO_2S_2^{=} + 0.1PO_3S^{=}$
3.0	A	
3.5	$0.3C + 0.4B + 0.3PO_3S$	$0.4B + 0.3C + 0.3PO_3S^{=}$

[a] The numbers in front of the letters or formulas designating chemical species represent the approximate fraction of the total phosphorus in that species (which may be a structure building unit). A is $PS_4^{=}$ or $POS_3^{=}$; B is probably a sulfur-free end group, ${}^{=}O_3PO_{1/2}^{-}$; C is probably a sulfur-free middle group, ${}^{-}O_2P(O_{1/2}^{-})_2$; X is probably a hydrolysis product of the completely sulfur-substituted phosphate branch group; Y is probably a hydrolysis product of the completely sulfur-substituted middle group.

The fact that chain and ring phosphates are found by paper chromatography in the aged hydrolysis products corresponding to Na_2S/P_2S_5 = 2.5, 3.0 and 3.5 indicates that hydrolysis of the orthothiophosphate glass involves polymerization, through formation of P–O–P linkages. Polymerization concomitant with hydrolysis has been observed previously for the polyphosphoryl chlorides[8] and, perhaps, for the polyphosphoramidates.[12] This means that it is difficult to visualize the original unhydrolyzed thiophosphate from knowledge of the hydrolysis fragments. Nevertheless, it would appear that the equilibrium[8] for exchange of roles between structure building units are such that K_1 is near zero and K_2 is considerably larger, perhaps being considerably larger than unity. (See eqs. 5 and 6 for the definition of K_1 and K_2.) The fact that only species A was observed for the glass exhibiting a Na_2S/P_2S_5 mole ratio of 3.0 immediately upon dissolution at 0° indicates that little or no free Na_2S is in equilibrium with the sodium phosphates so that K_3 is zero[13] or close to this value.

The substitution of sulfur for oxygen in the orthophosphates causes a negative chemical shift as shown in Table II. Shift increments are −32, −29, −25 and −1 p.p.m. for each successive replacement of oxygen by sulfur. The small shift increment observed upon replacement of the final oxygen atom has been demonstrated to be real, since both the trithio- and tetrathioorthophosphate anions were present in several solutions investigated so that partially overlapping but separate resonances were seen simultaneously for the two species.

Acknowledgments.—We wish to thank Wright Air Development Division, Air Research and Development Command, United States Air Force, Wright-Patterson Air Force Base, Ohio, for partial support of the work described herein under Contract AF 33(616)-6950. Gratitude is also due to Dr. L. C. D. Groenweghe for his kindness in reviewing and revising the figure in this paper and for determining the most probable values of the equilibrium constants.

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[12] *E.g.*, A. Narath, F. H. Lohman and O. T. Quimby, *J. Am. Chem. Soc.*, **78**, 4493 (1956).

[13] See pp. 724–731 of ref. 7. Also see J. R. Parks and J. R. Van Wazer, *ibid.*, **79**, 4890 (1957).

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Alkyl- and Arylsulfur Trifluorides[1]

BY WILLIAM A. SHEPPARD

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The first general synthesis of arylsulfur trifluorides has been found in the reaction of aryl disulfides with silver difluoride in 1,1,2-trichloro-1,2,2-trifluoroethane solvent. Fluorobutyl- and trifluoromethylsulfur trifluorides have been prepared by reaction of butyl disulfide and carbon disulfide or bis-trifluoromethyl trithiocarbonate with silver difluoride. The chemical and physical properties of the sulfur trifluoride compounds are described. In particular, the alkyl- and arylsulfur trifluorides have been shown to be useful reagents for selective conversion of carbonyl and carboxyl groups to difluoromethylene and trifluoromethyl groups.

Until recently, organic derivatives of sulfur fluorides were a relatively unknown class of compounds.[2] Numerous unsuccessful attempts to prepare RSF, RSF_3 and RSF_5 compounds have been reported.[3] In general the sulfur trifluoride compounds are known only with R as a perfluoroalkyl group and are prepared, usually in low yields, from organic sulfur compounds by reaction with elemental fluorine or by electrolytic fluorination in anhydrous hydrogen fluoride. For example, the derivatives of sulfur tetrafluoride, CF_3SF_3, $SF_5CF_2SF_3$, $F_3SCF_2SF_3$ and $F_3SCF_2CO_2H$, were prepared by fluorination of carbon disulfide and thioglycolic acid.[4] Recently Chamberlain and

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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 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

[2] For a recent review of compounds containing sulfur–fluorine bonds see H. L. Roberts, *Quart. Rev.*, **15**, 30 (1961).

[3] (a) H. J. Emeleus and H. G. Heal, *J. Chem. Soc.*, 1126 (1946). (b) R. N. Haszeldine in "Special Publication No. 12, Chemical Society Symposia," Bristol, 1958, The Chemical Society, Burlington House, W. I. London, 317 (see p. 331). (c) W. A. Sheppard and J. F. Harris, Jr., *J. Am. Chem. Soc.*, **82**, 5106 (1960).

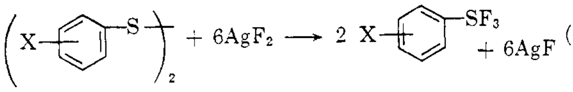
[4] (a) E. A. Tyczkowski and L. A. Bigelow, *ibid.*, **75**, 3523 (1953); (b) R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 2684 (1956).

Kharasch[5] prepared 2,4-dinitrophenylsulfur trifluoride by reaction of the corresponding disulfide in liquid hydrogen fluoride at 0° with fluorine diluted with nitrogen. Although a yield of 51% was obtained, this reaction was not applicable to the preparation of other arylsulfur trifluorides.

Sulfur tetrafluoride, the parent tetravalent sulfur fluorine compound, which is being studied extensively in this Laboratory,[6] is a selective reagent for conversion of carbonyl and carboxyl to difluoromethylene and trifluoromethyl groups.[6b]

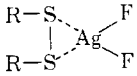
Results and Discussion

Preparation of Arylsulfur Trifluorides.—Phenylsulfur trifluoride is prepared in 60% yield by the exothermic reaction of phenyl disulfide with a suspension of silver difluoride in the "Freon" solvent, 1,1,2-trichloro-1,2,2-trifluoroethane (equation I, X = H). Phenylsulfur trifluoride is a colorless liquid, b.p. 60° (5 mm.), that slowly attacks glass but is stable indefinitely to storage at room temperature in a container made of an inert material such as "Teflon," polytetrafluoroethylene. By careful exclusion of moisture (normal Grignard reaction precautions), the preparation and distillation of phenylsulfur trifluoride may be carried out in "Pyrex" glass equipment. As a result of reaction with glass or with traces of moisture, the product was always found to contain a few per cent. of benzenesulfinyl fluoride as impurity. For preparation of pure samples of phenylsulfur trifluoride, "Teflon," copper, and stainless steel equipment is recommended but is less convenient and not readily available for laboratory use.


(I)

The "Freons" are valuable solvents for this reaction because they are inert to silver difluoride at the temperatures employed. In particular, 1,1,2-trichloro-1,2,2-trifluoroethane has a convenient b.p. of 47°. It was also observed qualitatively that phenylsulfur trifluoride does not attack glass as rapidly when dissolved in the "Freon" solvent as when in pure form or in benzene solution. Benzene was employed as a solvent in one preparation but was found considerably inferior to the "Freons."

Other common higher valence metal fluorides were not useful for the conversion of phenyl disulfide to phenylsulfur trifluoride. It was found that CoF_3, MnF_3, PbF_4 and HgF_2 were inert on warming with phenyl disulfide. On heating at higher temperatures only indiscriminate addition and substitution of fluorine occurred on the organic residue. In this respect the selective action of AgF_2 in fluorination of the sulfur atom without attack on the adjoining hydrocarbon group is without precedent. One explanation is that the sulfur coördinates with the silver atom so that the sulfur is in correct steric position for oxidative



fluorination, presumably by a radical type reaction. The AgF_2 is insoluble in the solvent or reactant and thus the disulfide may be adsorbed on the surface of the AgF_2 just prior to reaction. Although mercury normally coördinates strongly with sulfur, HgF_2 is not as reactive as AgF_2 in functioning as an oxidative fluorinating agent at temperatures below 100 to 200°.

The reaction of disulfides with silver difluoride provides a general method for preparation of arylsulfur trifluorides (equation I) where the substituent X on the organic nucleus is a group that is not sensitive to silver difluoride. In the present work, tolyl- and nitrophenylsulfur trifluorides were prepared in 30 to 50% yields. Aromatic thiols may also be employed as starting materials and the first step is the oxidation of the thiol to the disulfide by the silver difluoride. Hydrogen fluoride, formed as a by-product, must complex with the silver fluoride, since this reaction was run in a glass vessel without any significant etching of the glass.

Preparation of Alkylsulfur Trifluorides.—A study was made of the reaction of aliphatic disulfides with silver difluoride. *n*-Butyl disulfide gave the sulfur trifluoride derivative, $C_4H_8FSF_3$, with one fluorine in the aliphatic chain. On the basis of analysis and the F^{19} and H^1 n.m.r. spectra, this fluorine has been tentatively assigned to the α-position. From the mechanism for fluorination it would be predicted that an α-H would be in a preferred position for fluorination by silver difluoride. The lower aliphatic disulfides were also shown to react with silver difluoride, but the products could not be separated from the solvent by distillation. Benzyl disulfide and benzoyl disulfide both gave sulfur tetrafluoride and, respectively, benzal fluoride and benzoyl fluoride. In both cases the carbon–sulfur bond is extremely weak and cleavage during fluorination is not unexpected.

Trifluoromethylsulfur trifluoride was prepared in yields of 40–50% by passage of carbon disulfide or bis-(trifluoromethyl)-trithiocarbonate vapor diluted with nitrogen through a tube of loosely packed AgF_2. In the former reaction CF_3SF_5 was formed as the major by-product along with SF_4 and SF_6. In the latter case CF_3SSCF_3 was formed as the major by-product along with a minor amount of CF_3SF_5 and the parent sulfur fluorides. The reaction was exothermic, and by cooling the tube with an external water jacket the yield of CF_3SF_5 from CS_2 was lowered considerably, but the yield of CF_3SF_3 remained essentially unchanged.

Reactions of Sulfur Trifluorides.—The reactions of the alkyl- and arylsulfur trifluorides have been found to parallel those of sulfur tetrafluoride. The hydrolysis of phenylsulfur trifluoride to benzenesulfinic acid occurs with almost explosive violence and provides chemical proof for the sulfur tri-

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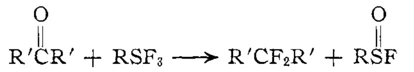
[5] D. L. Chamberlain, Jr., and N. Kharasch, *J. Am. Chem. Soc.*, **77**, 1041 (1955).

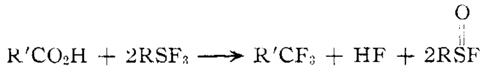
[6] (a) C. W. Tullock, F. S. Fawcett, W. C. Smith and D. D. Coffman, *ibid.*, **82**, 539 (1960). (b) W. R. Hasek, W. C. Smith and V. A. Engelhardt, *ibid.*, **82**, 543 (1960). (c) W. C. Smith, C. W. Tullock, R. D. Smith and V. A. Engelhardt, *ibid.*, **82**, 551 (1960).

fluoride structure. From the reaction of phenyllithium with phenylsulfur trifluoride in ether at −80°, only biphenyl and phenyl sulfide were isolated and none of the products expected from stepwise replacement of the fluorines by phenyl could be detected. The biphenyl and diphenyl sulfide no doubt arise from the decomposition of tetraphenylsulfur.[7] The conversion of arylsulfur trifluorides to the corresponding pentafluoride is discussed in the subsequent paper on arylsulfur pentafluorides[8] and provides additional chemical proof of structure.

The alkyl- and arylsulfur trifluorides, like SF_4, are useful reagents for conversion of carbonyl and carboxyl to difluoromethylene and trifluoromethyl groups. In particular, phenylsulfur trifluoride may be used to advantage in the labora-



$$R'\overset{\overset{O}{\|}}{C}R' + RSF_3 \longrightarrow R'CF_2R' + R\overset{\overset{O}{\|}}{S}F$$

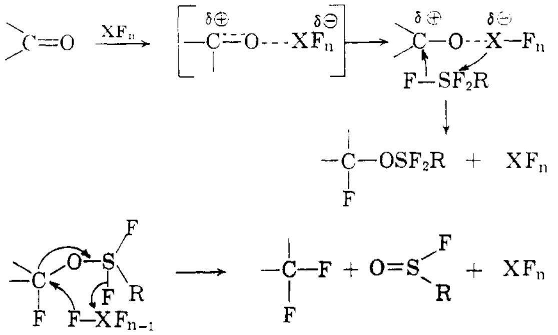


$$R'CO_2H + 2RSF_3 \longrightarrow R'CF_3 + HF + 2R\overset{\overset{O}{\|}}{S}F$$

tory for small scale preparations, since the reaction is run at atmospheric pressure in glass, polyethylene or metal containers. In contrast, sulfur tetrafluoride reactions require pressure equipment constructed of fluorine-resistant material, such as "Hastelloy-C" bombs.[6] One of the simplest reactions is that of phenylsulfur trifluoride with benzaldehyde. The reagents are mixed in equimolar portions and the products, benzal fluoride and benzenesulfinyl fluoride, distilled at reduced pressure. Benzenesulfinyl fluoride is a new compound representative of the class of sulfinyl fluorides that may be prepared by reaction of the sulfur trifluorides with carbonyl compounds. The sulfinyl fluorides are unstable to storage in glass at room temperature and appear to have properties similar to sulfinyl chlorides.

Considerable variation in reaction conditions is often needed with other types of carbonyl and with carboxyl groups. Aromatic ketones require heating with the sulfur trifluorides at 150° and a Lewis acid catalyst such as titanium tetrafluoride is advantageous. The reaction with aliphatic aldehydes and ketones is exothermic and is best controlled by use of a solvent such as methylene chloride or acetonitrile containing a small amount of sodium fluoride powder (with ketones an induction period of several hours may be observed). Carboxylic acids should be treated in a container resistant to hydrogen fluoride and require heating at 120 to 150°. A Lewis acid such as HF or BF_3 is an effective catalyst for the conversion of carbonyl to difluoromethylene groups with sulfur tetrafluoride. Since these catalysts are volatile, use of a nonvolatile catalyst such as titanium tetrafluoride is recommended for use with phenylsulfur trifluoride.

The relative reactivity of alkyl- and arylsulfur trifluorides compared to sulfur tetrafluoride is not readily determined because of the grossly different reaction conditions required for gaseous and liquid reagents. It is probable that the route by which an oxygen atom is replaced by two fluorine atoms is the same for alkyl- and arylsulfur trifluorides as for sulfur tetrafluoride. A possible mechanistic scheme is shown by (1) and (2).



(1)

(2)

It is believed that step 1 is rate controlling and that the catalytic activity of a Lewis acid results through coördination with the carbonyl group.[9] Step 2 is considered to be rapid, relative to (1), and may be analogous to the decomposition of chlorosulfites.[10] The reaction of phenylsulfur trifluoride with benzaldehyde provides a useful system for study of the mechanism of this reaction. The reaction proceeds at a convenient rate at normal temperatures and in a wide range of nonhydroxylic solvents. Considerable information can also be obtained on the effect of changing substituents on the aromatic rings of both reactants and on the function of Lewis acids as catalysts. In preliminary studies employing n.m.r. and infrared for analysis, it was shown that this reaction proceeds at a significantly faster rate in benzotrifluoride as solvent compared to the much less polar benzene and in the presence of sodium fluoride pellets.

Physical and Spectral Properties of Sulfur Trifluorides.—The physical properties of alkyl- and arylsulfur trifluorides are those that would be expected from sulfur tetrafluoride substituted with aliphatic and aromatic groups.[11] Phenylsulfur trifluoride has the strong odor often characteristic of aromatic sulfur compounds and similar to that of phenyl disulfide. Inhalation toxicity studies[12] have

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[7] (a) V. Franzen and C. Mertz, *Angew. Chem.*, **72**, 416 (1960), and *Ann.*, **643**, 24 (1961). (b) G. Wittig and H. Fritz, *Ann.*, **577**, 39 (1952).

[8] W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3064 (1962).

[9] Contribution of the Lewis acid in assisting the ionization of the fluoride from RSF_3 should also be considered. The fluoride may then be transferred from $\overset{\oplus}{RSF_2}\overset{\ominus}{XF_{n+1}}$. A bimolecular participation of RSF_3 through $\overset{\oplus}{RSF_2}\overset{\ominus}{RSF_4}$ is also possible if no Lewis acid is present.

[10] D. J. Cram, *J. Am. Chem. Soc.*, **75**, 332 (1953). It was suggested recently by L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 778, that the function of the catalyst is to promote step 2 by formation of a cyclic transition state as formulated above. However, if step 1 is rate controlling the function of the catalyst in this step is the important factor for accelerating the rate of reaction.

[11] The boiling point of phenylsulfur trifluoride (extrapolated to approximately 200° at atmospheric pressure) is much higher than those of benzotrifluoride (b.p. 103°) and phenylsulfur pentafluoride (b.p. 150°). These differences are in proportion to differences in boiling points for SF_4 compared with CF_4 and SF_6 and can be attributed to association of molecules occurring from weak intermolecular fluorine-to-sulfur bonding.

[12] The author is indebted to the Haskell Laboratory for Toxicology and Industrial Medicine, E. I. du Pont de Nemours and Company, for the toxicological data.

shown that phenylsulfur trifluoride is not as toxic as sulfur tetrafluoride or phosgene. However, it should be stressed that because of the ease with which phenylsulfur trifluoride is hydrolyzed with the liberation of hydrogen fluoride, the alkyl and arylsulfur trifluorides should be handled only with extreme precautions in a well ventilated area and should not be allowed in contact with the skin.

The infrared spectrum of phenylsulfur trifluoride is typical of a monosubstituted benzene except for a very strong absorption band at 807 cm.$^{-1}$. This is the most intense absorption in the spectrum in the range from 650 to 5000 cm.$^{-1}$ and has been assigned to the S–F stretching vibration. The *p*-nitrophenyl- and *p*-tolylsulfur trifluorides have similar strong absorptions at 813 cm.$^{-1}$. Also fluorobutylsulfur trifluoride has a strong absorption at 822 cm.$^{-1}$. Although there are no published spectra of sulfur trifluoride compounds,[13] it has been suggested that intense absorption between 860 and 910 cm.$^{-1}$ is diagnostic for a SF_3 group.[14] The ultraviolet spectrum of the arylsulfur trifluorides is that expected for an aromatic nucleus substituted with an electron-withdrawing group.[15]

The F^{19} nuclear magnetic resonance spectrum of phenylsulfur trifluoride[16] appears as a broad single resonance at low field. On cooling a dilute solution of phenylsulfur trifluoride in chloroform, the spectrum now appears as a doublet and triplet of intensity ratio two to one, respectively. The spectrum of SF_4 was examined recently from room temperature to $-85°$[17] and was shown to have a similar temperature effect with a single broad resonance at room temperature and two sets of triplets of equal intensity at low temperature. It was concluded that the SF_4 molecule possesses C_{2v} and not tetrahedral symmetry.[2,17] A similar conclusion about the structure of phenylsulfur trifluoride is drawn from the spectra. Since the rate of exchange is slowed by dilution with an inert solvent it is concluded, as was proposed for SF_4, that the exchange proceeds by a bimolecular process which can be explained by a dimer intermediate (Fig. 1) involving S–F bonding. Similar F^{19} spectra were found for the other alkyl- and arylsulfur trifluorides but with chemical shifts reflecting changes in shielding.

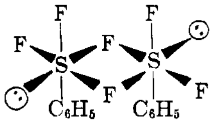

Fig. 1.

It is expected that the sulfur trifluoride group will be strongly electron withdrawing like the trifluoromethyl group and *meta*-directing for electrophilic substitution of the aromatic ring. A point of particular interest is the availability of the empty d-orbital on tetravalent sulfur for accommodation of extra electrons by resonance with an electron rich substituent. In addition, the unshared pair of electrons on sulfur may participate in a resonance interaction with electron withdrawing substituents. Unfortunately, because of the extreme reactivity of the SF_3 group, such measurements cannot be made by classical methods.

Experimental

Materials.—Silver difluoride (argentic fluoride) was purchased from the Harshaw Chemical Company. 1,1,2-Trichloro-1,2,2-trifluoroethane ("Freon 113"), b.p. 47°, was obtained from the Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware. Bis-trifluoromethyl trithiocarbonate, b.p. 110°, was prepared from bis-trifluoromethylthiomercury and thiophosgene.[18] All other reagents were purchased from Eastman Kodak Company or other chemical supply houses.

Preparation of Arylsulfur Trifluorides.—The following procedure for preparation of phenylsulfur trifluoride is representative of the method generally employed for the preparation of the arylsulfur trifluorides. The experimental details are given in Table I and the physical and analytical data on the arylsulfur trifluorides are summarized in Table II.

A 1-l., four-necked round-bottom flask equipped with a reflux condenser (protected from atmospheric moisture with a "Drierite" guard tube), sealed stirrer, thermometer and solid addition funnel was flushed with dry nitrogen and charged with 453 g. (3.1 moles) of silver difluoride and 500 ml. of 1,1,2-trichloro-1,2,2-trifluoroethane. Phenyl disulfide 100 g. (0.458 mole), charged in the solid addition funnel, was added to the stirred slurry in small portions. An exothermic reaction occurred on the addition of each portion of disulfide and after the addition of several portions the reaction temperature reached 40°. By intermittent use of a cooling bath and by adjusting the rate of addition of the disulfide, the reaction temperature was maintained between 35 and 40°. The addition of disulfide required approximately 60 minutes and on completion the exothermic reaction subsided and the black silver difluoride was almost completely converted to yellow silver monofluoride. The reaction mixture was stirred for an additional 15 to 30 minutes without external cooling, then quickly heated to reflux. The reaction mixture was filtered hot through a fluted filter paper under a blanket of dry nitrogen into a dry, 1-liter, round-bottom flask. The residue of solid silver fluoride was washed with a total of 500 ml. of boiling 1,1,2-trichloro-1,2,2-trifluoroethane in portions. The filtrate, an almost colorless solution, was freed of solvent by means of a short Vigreux column and the residue of phenylsulfur trifluoride was distilled at reduced pressure through a Claisen-type distillation column. The phenylsulfur trifluoride, b.p. 47–48° (2.6 mm.), was collected as a colorless liquid in a yield of 84–92 g. (56–61%). Since phenylsulfur trifluoride slowly attacks glass, it was found advantageous to keep all of the above manipulations in glass equipment to a maximum time of several hours. In contact with moisture or glass phenylsulfur trifluoride develops pink, green or bluish colors and was always found to contain a few per cent. of benzenesulfinyl fluoride. The phenylsulfur trifluoride was stored for several days in glass at $-80°$ or in polyethylene and was stored indefinitely at room temperature in bottles of "Teflon" or aluminum.

Preparation of Alkylsulfur Trifluorides.—The procedure described above for phenylsulfur trifluoride was used to prepare fluorobutylsulfur trifluoride. The experimental data are summarized in Table I and physical and analytical data in Table II.

In the preparation of trifluoromethylsulfur trifluoride a vapor phase reaction was employed. A stainless steel tube (2.5 × 76 cm.) was packed loosely with silver difluoride (lumps and powder) and the CS_2 or $(CF_3S)_2C{=}S$ vapor was carried into the tube in a He carrier gas stream. The products, trapped by use of liquid nitrogen and solid carbon dioxide,

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[13] The infrared spectrum of sulfur tetrafluoride has been analyzed by R. E. Dodd, L. A. Woodward and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 1052 (1956).

[14] L. H. Cross, G. Cushing and H. L. Roberts, *Spectrochim. Acta*, **17**, 344 (1961); see also ref. 8.

[15] The ultraviolet spectrum of phenylsulfur trifluoride, λ_{max} (ϵ): 275 (1180), 266 (1840), 261 (1940) cm.$^{-1}$ (ϵ in parentheses) is very similar to that of benzenesulfonyl fluoride, λ_{max} (ϵ): 273 (1150), 266 (1360), 260 (1950).

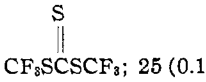
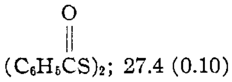
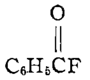
[16] A detailed study of these spectra with Dr. W. D. Phillips of this Laboratory is in progress.

[17] (a) F. A. Cotton, J. W. George and J. S. Waugh, *J. Chem. Phys.*, **28**, 994 (1958). (b) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

[18] R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3871 (1955).

TABLE I

REACTION OF ORGANIC SULFUR COMPOUNDS WITH SILVER DIFLUORIDE

Organic sulfur reactant, g. (mole)	AgF_2, g. (mole)	Solvent Cl_2FCCF_2Cl (ml.)	Product	Yield, %[a]
$(C_6H_5S)_2$; 100 (0.46)	453 (3.1)	500	$C_6H_5SF_3$	56–61
C_6H_5SH; 22.0 (0.20)	150 (1.0)	300	$C_6H_5SF_3$	51
$(4\text{-}CH_3C_6H_4S)_2$; 49.2 (0.20)	190 (1.3)	250	$4\text{-}CH_3C_6H_4SF_3$	57
$(4\text{-}O_2NC_6H_4S)_2$; 61.5 (0.20)	120 (0.82)	500[b]	$4\text{-}O_2NC_6H_4SF_3$[c]	22
$(2\text{-}O_2NC_6H_4S)_2$; 61.5 (0.20)	120 (0.82)	500[b]	$2\text{-}O_2NC_6H_4SF_3$[c]	25
$(n\text{-}C_4H_9S)_2$; 17.8 (0.10)	210 (1.5)	200	$n\text{-}C_4H_8FSF_3$	50
CS_2; 15 (0.20)	350 (2.4)	[d]	CF_3SF_3	48
			CF_3SF_5	20
			SF_4	40
			SF_6	12
CS_2; 15 (0.20)	350 (2.4)	[e]	CF_3SF_3	28
			CF_3SF_5	8
			SF_4	37
			SF_6	2
 $CF_3S\overset{S}{\overset{\|}{C}}SCF_3$; 25 (0.10)	100 (0.7)	[d]	CF_3SF_3	47
			 $CF_3\overset{O}{\overset{\|}{S}}F$	4
			CF_3SF_5	3
			CF_3SSCF_3	27
$(C_6H_5CH_2S)_2$; 20 (0.08)	115 (0.80)	200	$C_6H_5CF_2H$	35
			SF_4	20
 $(C_6H_5\overset{O}{\overset{\|}{C}}S)_2$; 27.4 (0.10)	145 (1.0)	200	 $C_6H_5\overset{O}{\overset{\|}{C}}F$	69
			SF_4	

[a] Based on organic sulfur compounds used as starting reagent. [b] Reaction not exothermic, required several hours refluxing. [c] Product crystallized from Freon solution after concentration. [d] AgF_2 packed loosely in 2.5 × 76 cm. stainless steel tube with support of 30 g. of 3.2 mm. NaF pellets at exit. CS_2 or CF_3CSSCF_3 vaporized in helium carrier gas flowing at rate of *ca.* 11 l./hour. Exothermic reaction, no external heating or cooling. [e] As in footnote *d* but tube cooled with copper condenser spiral tightly wrapped around tube. Condenser cooling liquid at −10°.

TABLE II

PROPERTIES OF ALKYL- AND ARYLSULFUR TRIFLUORIDES

R of RSF_3	B.p. (°C.)	M.p. (°C.)	Empirical formula and mol. wt.	Analyses[a] C Calcd.	C Found	H Calcd.	H Found	F Calcd.	F Found	S Calcd.	S Found
C_6H_5	47 (2.6 mm.)	*ca.* 0	$C_6H_5F_3S$, 166.2	43.3	44.6	3.04	3.24	34.3	33.5	19.3	19.9
$p\text{-}CH_3C_6H_4$	56 (1.0 mm.)	*ca.* 45	$C_7H_7F_3S$, 180.2	46.7	46.2	3.92	4.03	31.6	29.8	17.8	18.1
$4\text{-}O_2NC_6H_4$		*ca.* 56–58[b]	$C_6H_4F_3NO_2S$, 211.2	34.1	35.3	1.91	2.28	27.0	25.5	15.2	15.6
$2\text{-}O_2NC_6H_4$		*ca.* 50[b]	$C_6H_4F_3NO_2S$	34.1	35.9	1.91	2.16	27.0	25.7	15.2	15.1
CF_3[c]	−7										
$n\text{-}C_4H_8F$	78.5–80.5 (155 mm.)		$C_4H_8F_4S$	29.3	30.7	4.92	5.92	46.3	44.8	19.5	20.0

[a] All of the RSF_3 compounds contained a few per cent. (by n.m.r. analysis) RSOF as an impurity, even when extreme care was taken to minimize contact time of RSF_3 with glass and to exclude moisture. The relatively poor analyses (high carbon and low fluorine) are believed to result from this impurity and from difficulties in handling and burning compounds reactive with glass. [b] Recrystallization solvent, $Cl_2FCCClF_2$ or CCl_4. [c] Ref. 4a.

were distilled and analyzed by mass spectrometric and infrared techniques. There was a warm zone where the vapor first came in contact with the AgF_2 and this zone gradually moved down the tube as the reaction proceeded. In one experiment the reaction was cooled by a 6-mm. copper tube spiral condenser wrapped around the outside of the tube. The experimental details are summarized in Table I.

The results from fluorination of benzyl disulfide and benzoyl disulfide are also given in Table I.

Hydrolysis of Phenylsulfur Trifluoride.—Phenylsulfur trifluoride, 0.24 g., was added to 5 ml. of ice water. A vigorous reaction resulted and a white oily paste that formed immediately turned to a white powder after a few minutes. The solid was filtered (the filtrate gave a strong positive test for fluoride ion[19]) and dissolved in 5 ml. of 5% sodium hydroxide solution. The solution was washed with ether and acidified with 1 *N* sulfuric acid; the resulting white precipitate was triturated with ether. The ether solution was dried over anhydrous magnesium sulfate, filtered and evaporated under nitrogen. The residual white crystals, m.p. 76–77°, were shown by mixed melting point and infrared comparison to be identical with an authentic sample of benzenesulfinic acid, m.p. 76–78°, freshly prepared from sodium benzenesulfinate.

Reaction of Alkyl- and Arylsulfur Trifluorides with Carbonyl Compounds.—The experimental details of the reactions of the sulfur trifluoride compounds with carbonyl derivatives are summarized in Table III. The reaction of phenylsulfur trifluoride with benzaldehyde to give α,α-difluorotoluene and benzenesulfinyl fluoride is described in detail as an example of this type of reaction.

Phenylsulfur trifluoride (16.6 g., 0.10 mole) and 10.6 g. (0.10 mole) of benzaldehyde were mixed in a 50-ml. pot connected to a 45-cm. spinning-band column. A mild exothermic reaction was observed on mixing the reagents. The

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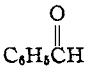
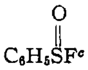
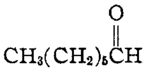
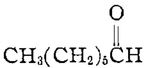
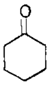
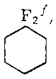
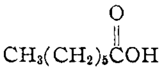
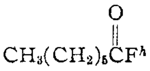
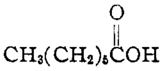
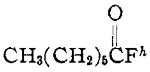
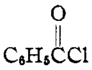
(19) J. H. Simons and E. O. Ramler, *J. Am. Chem. Soc.*, **65**, 389 (1943).

TABLE III

REACTIONS OF RSF_3 WITH CARBONYL COMPOUNDS

Carbonyl compound g. (mole)	RSF_3, g. (mole)	Conditions	Products[a]	Yield, %
 $C_6H_5\overset{O}{\overset{\parallel}{C}}H$ 10.6 (0.10)	$C_6H_5SF_3$ 16.6 (0.10)	Mixed at room temp.	$C_6H_5CF_2H$[b]  $C_6H_5\overset{O}{\overset{\parallel}{S}}F$[c]	71–80 82–89
 $CH_3(CH_2)_5\overset{O}{\overset{\parallel}{C}}H$ 11.4 (0.10)	$C_6H_5SF_3$ 17 (0.103)	Added RSF_3 dropwise to aldehyde; exothermic reaction	$CH_3(CH_2)_5CHF_2$[d]	21
 $CH_3(CH_2)_5\overset{O}{\overset{\parallel}{C}}H$ 11.4 (0.10)	$C_6H_5SF_3$ 20 (0.12)	Each reagent dissolved in 20 ml. of CH_2Cl_2. Added aldehyde solution dropwise to RSF_3 solution containing 3 g. NaF pellets, exothermic reaction	$CH_3(CH_2)_5CHF_2$[d]	38
$(C_6H_5)_2C{=}O$ 18.6 (0.10)	$C_6H_5SF_3$ 16.6 (0.10)	Catalyst: TiF_4 0.5 g. Heated in "Teflon" reactor at 150–160° for 2 hr., 185–205° for 3 hr.	$(C_6H_5)_2CF_2$[e] $(C_6H_5)_2C{=}O$	45 55
 3.1 (0.031)	$C_4H_8FSF_3$ 5.9 (0.033)	Allowed to stand overnight at room temperature in "Teflon" bottle		30
 $CH_3(CH_2)_5\overset{O}{\overset{\parallel}{C}}OH$ 6.5 (0.05)	$C_6H_5SF_3$ 17 (0.103)	Heated in "Teflon" reactor 110–125° for 2 hr.	$CH_3(CH_2)_5CF_3$[g]  $CH_3(CH_2)_5\overset{O}{\overset{\parallel}{C}}F$[h]	28 44
 $CH_3(CH_2)_5\overset{O}{\overset{\parallel}{C}}OH$ 13.0 (0.10)	CF_3SF_3 35 (0.20)	Heated in 145-ml. "Hastelloy"-lined bomb at 100° for 4 hr., 120° for 6 hr.	$CH_3(CH_2)_5CF_3$[g]  $CH_3(CH_2)_5\overset{O}{\overset{\parallel}{C}}F$[h]	28 20
 $C_6H_5\overset{O}{\overset{\parallel}{C}}Cl$	$C_6H_5SF_3$	Heated in "Teflon" reactor 5 hr. 100–115°	$C_6H_5CF_3$[i]	11

[a] All of the fluorocarbon products have been prepared previously by sulfur tetrafluoride reactions[6] and were characterized by comparison of physical properties and infrared and n.m.r. spectra with those of authentic samples. [b] B.p. 68° (80 mm.) and 45° (15 mm.). [c] B.p. 60° (25 mm.). The sulfinyl fluorides were not generally isolated because of instability during distillation and storage in glass. [d] B.p. 55–57° (76 mm.). [e] B.p. 99–103° (2.3 mm.). [f] B.p. 80–82.5° and 62° (190 mm.); $n^{25}D$ 1.384. [g] B.p. 101.5°. [h] B.p. 67° (75 mm.). [i] B.p. 103°.

reaction mixture was heated to 100° with an oil-bath and the pressure on the column was reduced until α,α-difluorotoluene distilled, b.p. 68° (80 mm.) and finally 45° (15 mm.), yield 9.2 to 10.2 g. (71–80%). The pressure was reduced and after an intermediate cut of 1 to 2 g., the benzenesulfinyl fluoride distilled, b.p. 60° (2.5 mm.), yield 11.7 to 13.2 g. (82–89%).

Anal. Calcd. for C_6H_5FOS: F, 13.2; S, 22.3. Found: F, 13.9; S, 21.9.

The infrared spectrum is very similar to that of phenylsulfur trifluoride but without the strong absorption at 807 cm.$^{-1}$. The F^{19} n.m.r. spectra show a single sharp resonance at −4992 c.p.s. at 56.4 Mc. (reference to $CFCl_2CFCl_2$ at 0 c.p.s.).

Spectral Properties of Alkyl- and Arylsulfur Trifluorides.—The ultraviolet spectrum of phenylsulfur trifluoride, as discussed above, is normal for a monosubstituted benzene derivative.[15] Because of the reactivity of the sulfur trifluoride compounds with glass, the ultraviolet spectra of the other aryl derivatives were not measured.

The infrared spectra of all the sulfur trifluorides reported in this study were as expected for the proposed structures. In all cases an intense absorption assigned to the S–F stretching frequency was observed at 807–813 cm.$^{-1}$ for the arylsulfur trifluorides. In the fluorobutylsulfur trifluoride spectrum a shift to higher frequency (822 cm.$^{-1}$) may result from the electronegative fluorine in the α-position.

The F^{19} n.m.r. spectrum is as follows (at 56.4 Mc./sec. reference to $CFCl_2CFCl_2$ at 0 c.p.s., in chloroform solution):

$C_6H_5SF_3$	(a) room temperature	−4992 c.p.s.
	(b) approx. −40°	−7882 c.p.s. (doublet, intensity 2)
		−2351 c.p.s. (triplet, intensity 1)

The chemical shifts and coupling constant for phenylsulfur trifluoride compared to those for sulfur tetrafluoride are:

$C_6H_5SF_3$; δ = 5531 c.p.s., J_{FF} = 53 c.p.s.

SF_4; δ = 2930 c.p.s., J_{FF} = 78 c.p.s.