m/e 266 (M^+), 338 (monosilylated product)$^+$, 410 (disilylated product)$^+$, 248 [monosilylated − $(CH_3)_3SiOH$]$^+$.

Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.24; H, 5.31; N, 10.53. Found: C, 71.15; H, 5.26; N, 10.34.

A mixture of 100 mg of **10** and 500 mg of activated MnO_2 in 10 ml of methylene chloride was stirred at 25° for 1 hr. Removal of MnO_2 and solvent yielded the yellow fluorescent maleimide, whose infrared spectrum was identical with an authentic sample of **4a**.

Registry No.—**2**, 675-75-2; **3a**, 53683-74-2; **3b**, 53683-75-3; **3c**, 53683-76-4; **3d**, 53683-77-5; **3e**, 53683-78-6; **3f**, 53683-79-7; **3g**, 53683-80-0; **4a**, 13797-26-7; **4b**, 24978-25-4; **4c**, 53683-81-1; **4d**, 53683-82-2; **4e**, 53683-83-3; **9**, 53683-84-4; **10**, 53683-85-5; **13**, 53683-86-6; **16**, 53683-87-7; aniline, 62-53-3; 4-fluoroaniline, 371-40-4; 2-fluoroaniline, 348-54-9; 4-methylaniline, 106-49-0; 4-chloroaniline, 106-47-8; 4-nitroaniline, 100-01-6; 2-nitroaniline, 88-74-4.

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Bromination and Chlorination of 1,1,1-Trifluoro-*N*-phenylmethanesulfonamides

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Bromination of aryl-substituted 1,1,1-trifluoro-*N*-phenylmethanesulfonamides in ethanol–water usually gave only one product when an extra equivalent of bromine was used to react with the acidic sulfonamide. Chlorination was much less selective and mixtures were always obtained. The (1,1,1-trifluoromethanesulfonyl)amino moiety was ortho–para directing in both cases. A number of halogen aryl substituted 1,1,1-trifluoro-*N*-phenylmethanesulfonamides were prepared by bromination and chlorination in higher overall yields than with prior syntheses which consisted of sulfonylation of the previously prepared halogenated aniline with trifluoromethanesulfonyl fluoride or anhydride. The chlorination of unsubstituted 1,1,1-trifluoro-*N*-phenylmethanesulfonamide was surveyed in various solvent–catalyst systems to prepare *N*-(2,4-dichlorophenyl)-1,1,1-trifluoromethanesulfonamide. The CH_3COOH–$AlCl_3$ and nitrobenzene–$AlCl_3$ systems gave the best selectivity with up to 70% 2,4-dichloro product produced in the latter system. Incremental addition of $AlCl_3$ to nitrobenzene during chlorination increased the rate of reaction and resulted in a mixture containing 81% 2,4-dichloro-, 10.4% 4-chloro-, and 8.6% 2,4,6-trichlorosulfonamide. Pure *N*-(2,4-dichlorophenyl)-1,1,1-trifluoromethanesulfonamide was then obtained by fractional crystallization in a yield of ~60%.

We have recently reported that halogen substituted 1,1,1-trifluoro-*N*-phenylmethanesulfonamides possess interesting and unique biological activity as herbicides and plant growth regulators.[1,2] The preparation of these compounds was generally by reaction of the substituted aniline with trifluoromethanesulfonyl fluoride or the corresponding anhydride. However, sulfonylations of di- and trihalogenated anilines were usually low yield reactions and often required usage of the more reactive and more expensive trifluoromethanesulfonic acid anhydride. In extreme cases, such as the preparation of *N*-(2,4,6-trichlorophenyl)-1,1,1-trifluoromethanesulfonamide, the sodium salt of the substituted aniline had to be preformed before sulfonylation could be effected.[2]

It has now been found that sulfonylation of mono- or unsubstituted anilines with trifluoromethanesulfonyl fluoride is generally a facile reaction (yields greater than 75%) and suitable starting materials are therefore readily available for subsequent halogenation. For this reason, halogenation of the parent and monosubstituted 1,1,1-trifluoro-*N*-phenylmethanesulfonamides was investigated as a possible alternate, higher yield route to the di- and trihalogenated compounds reported in this paper. Additionally, to the best of our knowledge, a careful study of the mixture of products resulting from halogenation of any alkanesulfonanilide previously had not been undertaken with presently available gas–liquid partition chromatography techniques.

The (methanesulfonyl)amino group has been shown to be an ortho–para director in electrophilic aromatic substitution. Shriner[3] in 1932 nitrated methanesulfonanilide with nitric acid in sulfuric acid and obtained only 2,4-dinitromethanesulfonanilide while Kostova[4] in 1959 treated ethanesulfonanilide in dichloroethane with chlorine and zinc oxide and obtained only 2,4-dichloroethanesulfonanilide. Low yields (5–10%) of other products probably would not have been detected because of the analytical procedures used by these authors. In addition, no attempt was made to moderate experimental conditions such that only monosubstitution would have occurred. More recently, the (1,1,1-trifluoromethanesulfonyl)amino moiety was shown to be an ortho–para director in the nitration of 1,1,1-trifluoro-*N*-phenylmethanesulfonamide.[5,6] However, the

Table I
Bromination of $XC_6H_4NHSO_2CF_3$ in 85% Ethanol–15% Water

X	Registry No.	Conditions[a]	Bromination Position	Registry No.	Mp (°C)	Yield (%)
H	456-64-4	30 min, 80°	4	23384-06-7	58–59	26.6
			2,4-di	23384-22-7	106–107	23.8
H		6 hr, reflux[b]	2,4-di		106–107	58.7
2-F	23383-98-4	30 min, 80°	4	53608-52-9	90.5–91.5	65.2
2-Cl	23384-02-3	30 min, 80°	4	53608-53-0	114.4–115.3	33.3
$2\text{-}CH_3$	53443-75-7	1 hr, reflux[c]	4	53608-54-1	88–90	88.7
4-F	23384-00-1	1 hr, 60°	2	53608-55-2	58–59	34.2
4-Cl	23384-04-5	45 min, 50°	2	53608-56-3	105–106	45.2
$4\text{-}CF_3$	23384-12-5	1.5 hr, reflux	2	53608-57-4	78–80	66.3

[a] Two moles of bromine per mole of sulfonamide unless specified otherwise. [b] Three moles of bromine per mole of sulfonamide. [c] Solvent, 63% ethanol–37% water.

Table II
Chlorination of $XC_6H_4NHSO_2CF_3$ with $AlCl_3$ as Catalyst

X	Solvent	Reaction Conditions	Chlorination Position	Registry No.	Mp or Bp (mm), °C	Approximate Composition (%)
2-F	Acetic acid	11 hr, 50°	4	53608-58-5	75–80 (0.05)	88
			4,6	53608-59-6	85–90 (0.05)	12
4-F	Acetic acid	56.5 hr, 50°	2	53608-60-9	75–78.5	75[a]
			2,6	53608-61-0	95–96	17
4-F	Acetic acid	8 hr, 100°	2,6		95–96	100
$4\text{-}CF_3$	Nitrobenzene	6 hr, 50°	2	27573-83-7	91.5–92.5	41[b]
			2,6	53608-62-1	109–111	57

[a] Includes 8% unreacted 1,1,1-trifluoro-*N*-(4-fluorophenyl)methanesulfonamide. [b] Includes 2% unreacted 1,1,1-trifluoro-*N*-(4-trifluoromethylphenyl)methanesulfonamide.

more electronegative di(1,1,1-trifluoromethanesulfonyl)amino group was shown to be predominately a meta directing group (89% meta–11% para nitration).[5]

Experimental Section

The preparations and physical properties of the aryl-substituted 1,1,1-trifluoro-*N*-phenylmethanesulfonamide starting materials and all of the mono-, di-, and trichlorinated 1,1,1-trifluoro-*N*-phenylmethanesulfonamides were reported previously as was the general procedure for sulfonylation of substituted anilines with trifluoromethanesulfonyl fluoride.[2] All new compounds had satisfactory carbon, hydrogen, and nitrogen microanalyses (±0.3%) and infrared spectra. All melting points are uncorrected.

General Bromination Procedure. Bromine (3 mol) was added dropwise at room temperature to a solution of the 1,1,1-trifluoro-*N*-phenylmethanesulfonamide (1 mol) in 85% ethanol–15% water. The solution warmed to about 35° during the addition. The solution was refluxed until the bromine color was discharged (6 hr). The reaction mixture was cooled and poured into ice–water and the crystals were filtered. Recrystallization was from hexane–benzene.

General Chlorination Procedure. Chlorine, dried with concentrated sulfuric acid, was passed through a calibrated flowmeter into a nitrogen flushed, mechanically stirred, and electrically heated solution of the sulfonamide. The reaction was initially exothermic in acetic acid. With acetic acid solvent, the mixture was poured into ice–water and the resulting oil extracted twice with dichloromethane. With sodium hydroxide and water as solvent, the final acidic reaction mixture was extracted directly. Product recoveries were nearly quantitative because of the high lipophilicity of the various sulfonamides. With nitrobenzene solvent, the acidic sulfonamides were extracted with sodium hydroxide solution after addition of petroleum ether to decrease the solubility of the sodium salt in the organic phase.

Gas–Liquid Partition Chromatography. Product analyses were by a Varian Aerograph 202B gas chromatograph. The 0.25 in. o.d. column was packed with 7 in. of 15% XE60 on ABS followed by 3 ft of 25% QF1 on Anakrom P. The helium pressure was 50 cm^3/min and the column temperature was 205°.

Results

Preparative Brominations. The bromination reactions are summarized in Table I. There was no indication of more than one product even when examined by glpc except as noted for the bromination of 1,1,1-trifluoro-*N*-phenylmethanesulfonamide (1). Bromination of 1 with 1 equiv of bromine gave an oil upon reaction work-up. This oil was an unseparable mixture of largely starting material and a small amount of the 4-brominated product (estimated from the infrared spectrum). However, bromination of 1 with 2 equiv of bromine gave an easily separable mixture of 4-bromo (oil) and 2,4-dibromo (crystalline) derivatives in the yields given in Table I. Bromination of 1 with 3 equiv of bromine resulted only in 2,4-dibromination.

Preparative Chlorinations. These reactions are summarized in Table II. The chlorination reactions were not as selective as were brominations since it was impossible to obtain only monochlorination. Product percentages are approximate since detector response factors were not determined. Pure products were obtained by preparative glpc utilizing a Beckman Megachrom^R chromatograph equipped with a 0.75 in. o.d. column packed with 12 ft of 25% SE-30 on Chromosorb P. The helium pressure was 1.5 psi and the column temperature was 200°.

Chlorination of 1,1,1-Trifluoro-*N*-phenylmethanesulfonamide (1). The chlorination of 1 was investigated in more detail as a preparative procedure for obtaining *N*-(2,4-dichlorophenyl)-1,1,1-trifluoromethanesulfonamide. This compound is a novel herbicide and plant growth regulator which had been prepared previously in low yields (3.4%) by the sulfonylation of 2,4-dichloroaniline.[2] The effect of solvent and catalyst was first surveyed and the results of the initial survey are shown in Table III. All of the possible chlorinated products had previously been prepared by other means and detector response factors were used to calculate exact product composition percentages.

The more active solvent–catalyst systems such as CCl_4–$AlCl_3$ and NaOH–water produced a more random mixture and a larger amount of the undesired 2,4,6-trichloro product. The NaOH–water system was also undesirable since evolved hydrochloric acid neutralized the sodium hydrox-

Table III
Survey of Effect of Catalyst (0.5 g) and Solvent (50 ml) on Chlorination of $C_6H_5NHSO_2CF_3$ (0.05 mol)

Catalyst	Solvent	Temp (°C)	Time (hr)	Total Chlorine (mol)	Composition (%) Starting Material	2-Cl	4-Cl	2,4-diCl	2,6-diCl	2,4,6-triCl
$CuCl_2$	CH_3COOH	60	2	0.20	0	19.0	65.2	14.7	0.1	0.7
$ZnCl_2$	CH_3COOH	50	2	*a*	1.1	18.9	73.7	4.7	0	1.6
$FeCl_3$	CH_3COOH	50	2	*a*	0	16.8	60.8	19.4	1.2	1.9
$AlCl_3$	$CHCl_3$	50	2	0.44	16.3	3.3	57.2	19.9	0.2	2.9
$AlCl_3$	CCl_4	50	2	0.44	0	22.0	62.0	5.8	0	10.2
$AlCl_3$	CH_3COOH	70	1.5	0.33	0	10.5	57.0	29.9	0.1	2.5
$AlCl_3$	Nitrobenzene	50	3	*a*	0	5.7	44.0	44.2	0.8	5.3
	$NaOH/H_2O$[b]	40	1	0.17	0	15.0	15.3	50.3	11.2	8.2
S_2Cl_2	CH_3COOH	50	2	0.44	0	10.0	79.0	7.0	4.0	Trace

[a] Not measured. [b] Used 0.0525 mol of NaOH.

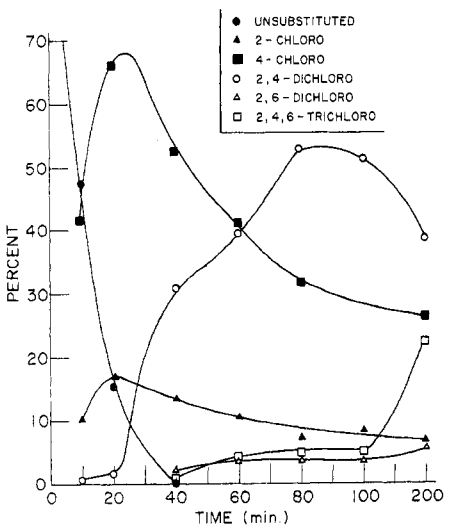


Figure 1. Chlorination of 1 (0.05 mol) in acetic acid (50 ml)–$AlCl_3$ (0.5 g) at 20° (0.22 mol of Cl_2/hr).

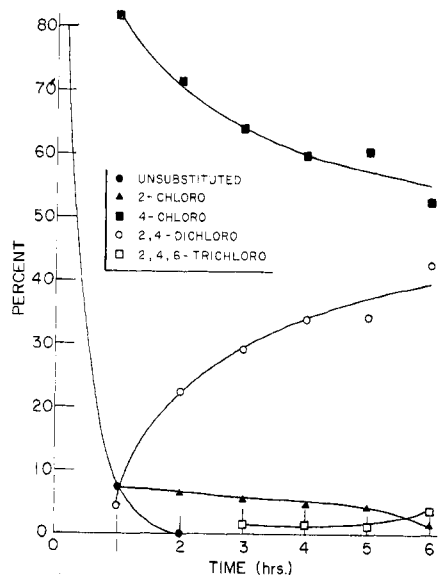


Figure 2. Chlorination of 1 (0.125 mol) in nitrobenzene (160 ml) at 50° (0.47 mol of Cl_2/hr).

ide resulting in precipitation of the sulfonamides making the reaction heterogeneous. Primarily 4-chloro and 2,4-dichloro products were produced in the less active systems such as CH_3COOH–$AlCl_3$ and nitrobenzene–$AlCl_3$ and these systems were investigated in more detail. In all these solvent–catalyst systems, pure 4-chloro-1,1,1-trifluoromethanesulfonamide could be isolated by fractional recrystallization in yields of greater than 50% if chlorination times were reduced.

The product ratios as a function of time were determined by glpc for the solvent–catalyst system CH_3COOH–$AlCl_3$. These results are plotted in Figure 1. In this system the concentration of the 2,4-dichloro product never exceeded 52.5% since the 2,4,6-trichloro concentration became large before all of the 2-chloro and 4-chloro products were consumed. The chlorination of 1 in nitrobenzene (no catalyst) at 50° was slow as shown in Figure 2. The addition of $AlCl_3$ (0.09 mol/mol of sulfonamide) resulted in only a slight rate increase at 50° and had a negligible effect upon product ratios. However, in nitrobenzene–$AlCl_3$ at 80° an increased reaction rate was observed, and results are shown in Figure 3.

A significant improvement of the nitrobenzene–$AlCl_3$ over the CH_3COOH–$AlCl_3$ system is that the concentration of 2,4,6-trichloro product did not increase significantly with time in the former system. In order to further increase the rate of chlorination in nitrobenzene, 0.15 mol of $AlCl_3$ for each mole of 1 was added at the beginning and after 3.5 hr of chlorination. At the end of 6.5 hr, the reaction mixture contained approximately 81% 2,4-dichloro, 10.4% 4-chloro, and 8.6% 2,4,6-trichloro products. Pure 2,4-dichloro product was then obtained by fractional recrystallization in yields of approximately 60%.

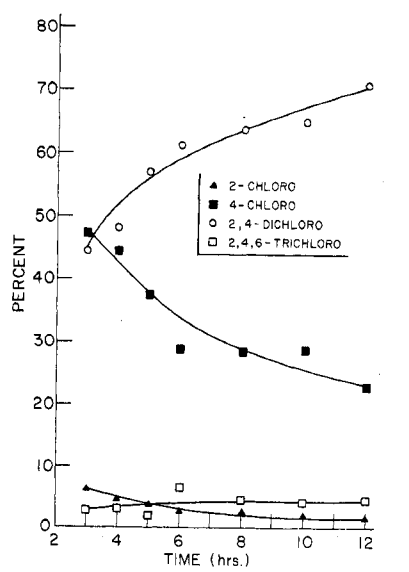
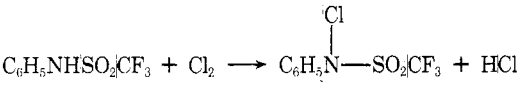


Figure 3. Chlorination of 1 (0.125 mol) in nitrobenzene (160 ml)–$AlCl_3$ (1.5 g) at 80° (0.30 mol of Cl_2/hr).

Discussion and Conclusions. In the halogenation of sulfonamides, the first equivalent of halogen probably

reacts at the acidic (1,1,1-trifluoromethanesulfonyl)amino site (pK_a = 4.45 for **1**)[1] as illustrated for the chlorination of



1. Attempts to isolate such an intermediate in this study were unsuccessful. Such intermediates have been isolated from numerous aryl-substituted *N*-phenylbenzenesulfonamides[7] and *N,N*-dichloroalkanesulfonamides have also been prepared.[8] The former compounds rearrange in glacial acetic acid to give ortho–para ring chlorination. In addition, further chlorination of the *N*-chloro-*N*-phenylbenzenesulfonamides with sodium hypochlorite in glacial acetic acid results in the formation of *N*-chloro-*N*-(2,4,-dichlorophenyl)benzene sulfonamide.[7] Therefore the directing group in the present study is probably an *N*-halogen-(1,1,1-trifluoromethanesulfonyl)amino moiety which is clearly an ortho–para directing group as indicated by the results shown in Tables I and II.

In the present study bromination of 1,1,1-trifluoro-*N*-phenylmethanesulfonamides was found to be much more selective (only 2,4-dibromination with 3 equiv of bromine) than was chlorination. Both bromination and chlorination of aryl-substituted 1,1,1-trifluoro-*N*-phenylmethanesulfonamides result in higher overall yields when compared with the previous syntheses[2] and require less expensive starting materials. The halogenation technique also allowed syntheses of sulfonamides in cases where the corresponding di- or trihalogenated anilines were not commercially available. These anilines could have been prepared by conventional techniques but the subsequent sulfonylations would then have been low yield reactions as previously described.

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Registry No.—Bromine, 7726-95-6; chlorine, 7782-50-5.

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On The Alkylation of Multisite Aromatic Heterocycles. 1,2,3,4-Thiatriazoles

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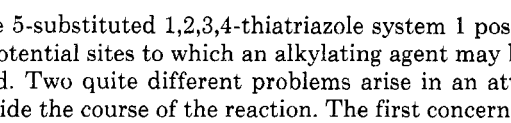
5-Substituted 1,2,3,4-thiatriazoles are alkylated with triethyloxonium tetrafluoroborate to give a single product. The location of the ethyl group in the ring at position 3 has been accomplished by means of ^1H, ^{15}N, and ^{13}C nmr. CNDO calculations were performed to rationalize the exclusive alkylation of nitrogen β to sulfur. The theoretical and experimental results are in conflict, suggesting that the reaction is more complicated than it appears.

The 5-substituted 1,2,3,4-thiatriazole system **1** possesses five potential sites to which an alkylating agent may be delivered. Two quite different problems arise in an attempt to decide the course of the reaction. The first concerns substituent *vs.* ring attack. The second arises in the latter case and involves a decision as to which heteroatom of **1** has been alkylated. It is to these questions that we primarily address ourselves in the sequel.



1a, X = SCH_2CH_3 **2a**, X = SCH_2CH_3
b, X = SCH_3 **b**, X = SCH_3
c, X = C_6H_5 **c**, X = C_6H_5

Treatment of sodium 1,2,3,4-thiatriazole-5-thiolate (**1**, X = S^-) with diphenylmethyl, triphenylmethyl, and benzoyl chloride were formerly believed to yield 4-substituted 1,2,3,4-thiatriazoline-5-thiones.[2] In a recent paper these reactions were reexamined and evidence was presented that the products obtained in fact are all 5-substituted 1,2,3,4-thiatriazoles.[3] On the other hand it was reported by Neidlein and Tauber that alkylation of 5-arylamino-1,2,3,4-thiatriazoles (**1**, X = NHAr) with diazomethane leads to formation of 4-methyl-5-arylimino-1,2,3,4-thiatriazolines, while alkylation with dimethyl sulfate provides 5-*N*-aryl-*N*-methylamino-1,2,3,4-thiatriazoles.[4] These results prompted us to investigate the reaction of 5-mercapto-1,2,3,4,-thiatriazole (**1**, X = SH) with diazomethane and triethyloxonium tetrafluoroborate. Only the 5-alkylthio-1,2,3,4-thiatriazoles are formed.

By contrast the latter products, **1a** and **1b**, as well as 5-phenylthiatriazole (**1c**), can be alkylated with $Et_3O^+BF_4^-$ yielding crystalline salts. Under similar alkylating conditions, the alkoxy derivative (**1**, X = OC_2H_5) decomposes entirely to nitrogen, sulfur, and ethyl cyanate as previously described.[5] Apparently the electronegative ethoxy moiety reduces electron density in the ring sufficiently so that alkylation cannot compete with fragmentation.

The structures of the former salts are analyzed below on the basis of ^1H, ^{13}C, and ^{15}N nmr data.

S *vs.* N Alkylation. Upon treatment with triethyloxonium tetrafluoroborate the 5-ethyl- and 5-methylthio derivatives of **1** (**a, b**) lead to a single product salt in each case in 65 and 35% yields, respectively. The ^1H nmr values of starting thiatriazoles and the corresponding ethyl derivatives are given in Table I.

Ring alkylation is immediately suggested since the ethyl