spectrum showed absorption at 6.05 μ (carbonyl) and the nmr spectrum exhibited only aromatic proton absorption, a 6 H multiplet at δ 7.8–8.1 and a 14 H muliplet at 7.0–7.5.

Anal. Calcd for $C_{29}H_{20}O_3$: C, 83.65; H, 4.81; mol wt, 416. Found: C, 83.39; H, 4.81; mol wt, 420, 415.

Reduction of 2-Benzoyl-1,3,5-triphenyl-2-butene-1,4-dione (9).—A sample of **9** (0.43 g, 0.001 mol) and 0.41 g (0.006 mol) of zinc powder were refluxed in 50 ml of glacial acetic acid for 1 hr. The reaction mixture was added to water and extracted with ether. Acetic acid was removed by extraction with 5% sodium hydroxide solution until the extracts were alkaline. The ethereal solution was washed with water, dried over calcium chloride, and evaporated to yield a residue (0.34 g, 85% yield), mp 168–172°. On recrystallization from ethanol, pale yellow crystals (mp 175–176°) were obtained that were identified as **1** from mixture melting point and spectral data.

2-Benzoyl-1,3,4-triphenylbutane-1,4-dione (14).—Sodium hydride (1.2 g, 0.028 mol), 56% by weight in mineral oil, was washed three times with small quantities of petroleum to remove the mineral oil, and added, under nitrogen, to a flask containing 150 ml of anhydrous 1,2-dimethoxyethane. ω-Desylacetophenone[19] (8.0 g, 0.026 mol) was added and the system was heated at 55° until the evolution of hydrogen gas had ceased (45 min). Vigorous evolution of gas occurred only near the end of the reaction. Benzoyl chloride, 1.75 g (0.01 mol), in 25 ml of 1,2-dimethoxyethane, was added dropwise to the dark-red solution. The reaction mixture was heated for 30 min and poured onto cracked ice. After acidification, the reaction mixture was extracted with ether. The ether solution was extracted with 5% sodium hydroxide solution until the extracts produced no more solid on acidification. The alkaline extracts were combined, acidified, and extracted with ether. The ethereal solution was washed with water, dried over calcium chloride, and evaporated to yield 3.07 g (58% yield) of **14**, mp 164.5–165° (from ethyl ether). The infrared spectrum showed carbonyl absorption at 5.95 and 6.05 μ. The nmr spectrum revealed 1 H (methinyl) doublets centered at δ 6.33 and 5.73 ($J \cong 5.1$ cps) and a 20 H (aromatic) multiplet at 6.8–8.0.

Anal. Calcd for $C_{29}H_{22}O_3$: C, 83.25; H, 5.26. Found: C, 83.22; H, 5.21.

The ether solution remaining after alkaline extraction was washed with water, dried over calcium chloride, and evaporated. Recrystallization of the residue gave 3.95 g (99% recovery) of ω-desylacetophenone, mp 124–126° (lit.[19] mp 126°).

Dehydration of 2-Benzoyl-1,3,4-triphenylbutane-1,4-dione (14).—A sample of **14** (1.0 g, 0.0024 mol) and 6.0 ml of concentrated hydrochloric acid were refluxed in 200 ml of ethanol for 2.5 hr. After evaporation of solvent, the residue was triturated with ethanol to yield 0.83 g (87% yield) of pale yellow solid, mp 175–176° (from ethanol). On admixture with **1**, no depression was observed in the melting point. The infrared spectra of the two samples were identical.

Registry No.—**1**, 15440-99-0; **2**, 13249-75-7; **3**, 13810-16-7; **4** (R = R′ = Ph), 134-81-6; **8**, 15441-02-8; **9**, 15441-03-9; **14**, 15441-04-0; phenoxide ion, 3229-70-7.

Acknowledgments.—We are grateful to Dr. M. R. Willcott of the University of Houston for obtaining the nmr spectra. We also acknowledge the assistance of Mr. James Doty and Mr. Tommy Wilbanks who prepared some of the starting materials.

Directive Effects in the Chlorination of Benzyl Chloromethyl Sulfides[1]

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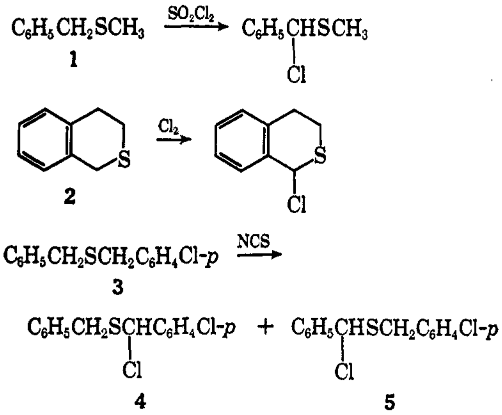
A series of benzyl chloromethyl sulfides has been prepared and treated sequentially with sulfuryl chloride and *m*-chloroperbenzoic acid. Separation and analysis of the resulting chloro sulfone mixtures have established the much greater directing influence of a chlorine atom when compared with a substituted phenyl group, except when the aromatic ring carries a *p*-nitro substituent.

When a sulfide possessing at least one hydrogen at an α-carbon atom is treated with 1 equiv of chlorine,[4] sulfuryl chloride,[5,6] or N-chlorosuccinimide (NCS)[1,7] in an inert solvent, α-chloro sulfides are produced. Addition of larger amounts of chlorinating agent generally results in more extensive halogenation.[6a,8] A major portion of the interest associated with this reaction derives from the unresolved nature of the detailed mechanism involved in the α-chlorination process.[5,6,9]

Only a limited number of isolated reports have appeared concerning directive effects in the chlorination of sulfides. Thus, chlorination of benzyl alkyl sulfides such as **1**[10] and **2**[11] has been shown to lead only to α-chlorobenzyl sulfides. Chlorinated isomers **4** and **5** are formed in the ratio of 1.6:1 when benzyl *p*-chlorobenzyl sulfide (**3**) is treated with an equimolar quantity of N-chlorosuccinimide in carbon tetrachloride solu-



$$\underset{\mathbf{1}}{C_6H_5CH_2SCH_3} \xrightarrow{SO_2Cl_2} C_6H_5\underset{Cl}{\underset{|}{C}}HSCH_3$$

$$\underset{\mathbf{3}}{C_6H_5CH_2SCH_2C_6H_4Cl\text{-}p} \xrightarrow{NCS}$$

$$\underset{\mathbf{4}}{C_6H_5CH_2S\underset{Cl}{\underset{|}{C}}HC_6H_4Cl\text{-}p} + \underset{\mathbf{5}}{C_6H_5\underset{Cl}{\underset{|}{C}}HSCH_2C_6H_4Cl\text{-}p}$$

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(1) α-Halo Sulfones. Paper IX. For previous paper in this series, see L. A. Paquette and J. C. Phillips, *Tetrahedron Lett.*, 4645 (1967). The authors wish to express their appreciation to the National Science Foundation for funds used in partial support of this Research Fellow, 1965–1967.

(2) Alfred P. Sloan Foundation Research Fellow, 1965–1967.

(3) Undergraduate research participant, 1965–1966.

(4) H. Böhme, H. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949), and pertinent references cited therein.

(5) (a) F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955); (b) F. G. Bordwell, G. D. Cooper, and H. Morita, *ibid.*, **79**, 376 (1957).

(6) (a) W. E. Truce, G. H. Birum, and E. T. McBee, *ibid.*, **74**, 3594 (1952); (b) L. A. Paquette, *ibid.*, **86**, 4085 (1964).

(7) (a) D. L. Tuleen and T. B. Stephens, *Chem. Ind.* (London), 1555 (1966); (b) D. L. Tuleen and V. C. Marcum, *J. Org. Chem.*, **32**, 204 (1967).

(8) (a) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4089 (1964); (b) L. A. Paquette and L. S. Wittenbrook, *ibid.*, **89**, 4483 (1967); (c) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967); (d) L. S. Wittenbrook, unpublished observations.

(9) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p 59.

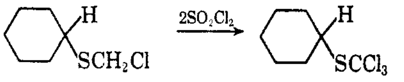
(10) F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **73**, 5187 (1951).

(11) H. Böhme, L. Tils, and B. Unterhalt, *Chem. Ber.*, **97**, 179 (1964).

tion.[7b] Polychlorination of dimethyl sulfide results in all the hydrogens of one carbon atom being replaced by chlorine before the second methyl group is attacked.[6a] The same substitution behavior is displayed by chlorosulfides **6**[8c] and **7**.[8d] Whereas reaction of dibenzyl sulfide with 2 equiv of sulfuryl chloride produces the α,α-dichloro sulfide as the only product,[8a] it has been observed that 2,7-dihydro-3,4-5,6-dibenzothiepin (**8**) interestingly affords a mixture of **9** and **10** in a ratio of 3.6:1 (based upon the isolation of pure dichloro sulfones) under the same conditions;[8a] in the latter case, it has been proposed that the strong inductive effect of the α-chloro substituent in the intermediate α-chloro sulfide is offset by steric factors operative in the transition state for α,α-dichlorination leading to substitution in the opposite direction. The present study describes directive effects operative in the sulfuryl chloride chlorination of a group of selected benzyl chloromethyl sulfides in which structural modifications have been introduced to provide additional insight into the requirements of such competitive proton abstraction processes and the mechanism of halogenation.

$$C_6H_5CH_2SCH_2Cl \xrightarrow{SO_2Cl_2} C_6H_5CH_2SCHCl_2$$

6



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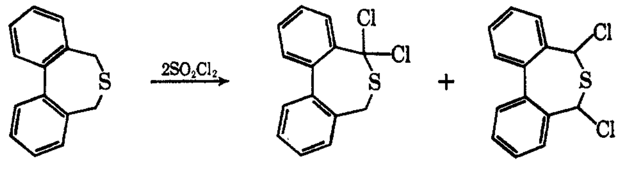
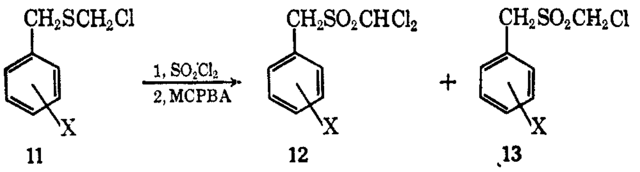


8 **9** **10**

Results and Discussion

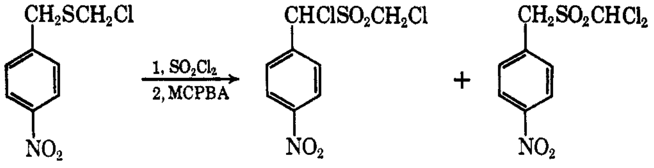
The sequential reaction of chloromethyl p-fluorobenzyl sulfide (**11a**) with 1 equiv of sulfuryl chloride and excess m-chloroperbenzoic acid (MCPBA) in chloroform solution afforded a mixture consisting of **12a** (80%) and **13a** (20%). Chlorination of chloromethyl p-chlorobenzyl sulfide (**11b**) and chloromethyl m-trifluoromethylbenzyl sulfide (**11c**) under similar conditions produced dichloro sulfones **12b** and **12c**, respectively, as the only dichlorinated products. No evidence of halogenation at the benzylic methylene group was detected upon close examination of the nmr spectra of the crude reaction mixtures before and after oxidation. The mono- and dichloro sulfones were identified by elemental analysis and by their nmr and mass spectra. The chemical shifts of the various α-sulfonyl proton absorptions which are collected in Table I are seen to be unexceptional for these six compounds when the shielding constant for chlorine is taken into consideration. The electron-impact-induced fragmentations of **12b** and **12c** were found to result predominantly in direct cleavage of the benzylic C–S bond to give the corresponding tropylium cations. Thus, the mass spectrum of **12b** displayed a base peak at m/e ($C_7H_6Cl^+$) and that of **12c** a base peak at m/e 159 ($C_8H_6F_3^+$). No other peaks of greater than 15% relative intensity were observed.[12]



11 **12** **13**

a, X = p-F; b, X = p-Cl; c, X = m-CF$_3$

In contrast to the above results, when chloromethyl p-nitrobenzyl sulfide (**14**) was treated with 1 molar equiv of sulfuryl chloride and the crude mixture of dichloro sulfides was oxidized directly with MCPBA, the isomeric dichloro sulfones **15** and **16** were formed in a ratio of 3:2. The nmr spectra of **15** and **16** (Table I) are closely related to those of compounds with similar structures. With particular regard to the spectrum of **15**, it should be noted that the protons of the methylene group appear as an AB pair of doublets. The nonequivalency of these protons, presumably caused by the spatial proximity of the asymmetric benzylic carbon atom, has been observed with a limited number of sulfones.[13] In further confirmation of the structural assignments, the mass spectrum of **16** was found to exhibit a base peak at m/e 136 ($C_7H_6NO_2$)$^+$ as expected from the analogous fragmentation of chloromethyl p-nitrobenzyl sulfone. The mass spectrum of **15** is clearly seen to be that of an α-chloro-p-nitrobenzyl sulfone because of the base peak at m/e 170 ($C_7H_5ClNO_2^+$).



14 **15** **16**

TABLE I

CHEMICAL SHIFTS OF BENZYLIC AND NONBENZYLIC α-SULFONYL PROTON(S) IN SELECTED α-CHLORINATED SULFONES[a]

Compd	δ, ppm Benzylic	Nonbenzylic
Dibenzyl sulfone	4.10	
$C_6H_5CH_2SO_2CHClC_6H_5$	4.44	(5.42)
13a	4.41	4.26
13b	4.37	4.21
13c	4.46	4.27
p-$NO_2C_6H_4CH_2SO_2CH_2Cl$	4.53	4.32
$C_6H_5CH_2SO_2CHCl_2$	4.56	6.04
12a	4.51	6.03
12b	4.53	6.06
12c	4.58	6.10
16	4.71	6.22
15	6.13	4.51, 5.10[b]
18		5.12
17	4.88	
$C_6H_5CH_2SO_2CCl_3$	4.77	

[a] Spectra were determined on *ca.* 15% solutions in $CDCl_3$; values are reported relative to internal tetramethylsilane and refer to singlets unless otherwise indicated. [b] AB pattern, J_{AB} = 13 Hz.

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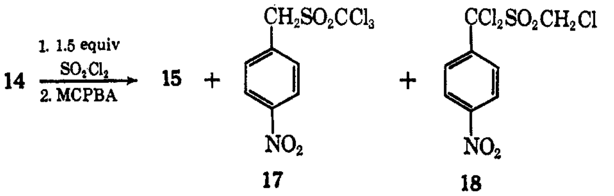
[12] The favored fragmentation of sulfones to give R^+ and RSO_2^+ has been recognized previously: R. T. Aplin and K. Bailey, *J. Chem. Soc., Sect. B*, 513 (1967), and appropriate references cited therein.

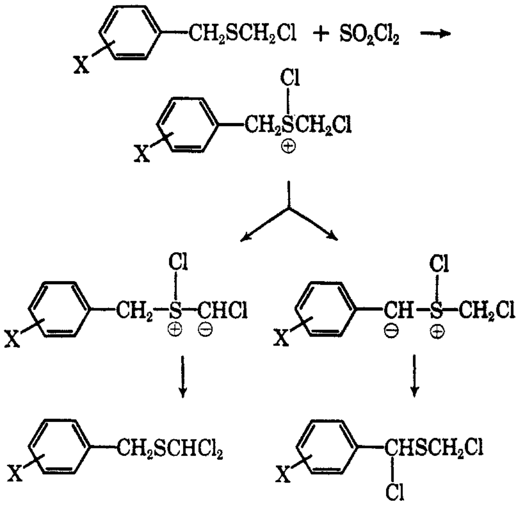
[13] J. J. Looker, *J. Org. Chem.*, **31**, 2973 (1966); see also ref 7b.

Chlorination of **14** with an excess (1.5 molar equiv) of sulfuryl chloride led after oxidation to a mixture of **15** (54%) and the isomeric trichloro sulfones **17** (38%) and **18** (8%). Assignment of structure to **17** and **18** again rests on their nmr and mass spectra. Whereas **17** produces a base peak at *m/e* 136 ($C_7H_6NO_2^+$) upon electron impact, trichloro sulfone **18** is seen to undergo extensive fragmentation (base peak *m/e* 43).

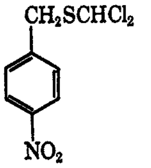


17 **18**

The data presented here definitively establish the much greater directing influence of a chlorine atom when compared with a substituted phenyl group, except when the aromatic ring carries a *p*-nitro substituent. Even in this case, however, a more or less equitable situation obtains (ratio 1.5:1). Although the observed directive effects are inconsistent with the suggestion of Price and Oae[9] that the chlorination of sulfides by sulfuryl chloride may proceed by means of an intermediate radical stabilized by octet expansion of the adjacent sulfur atom, they do agree with the intervention of an ionic mechanism. Subsequent to S-chlorosulfonium salt formation, the more acidic α hydrogen is subject to abstraction and the resulting ylide is transformed to the observed α-chloro sulfide. On this basis, the nature of the products would be expected to be controlled by the relative acidities of the α protons which, in turn, reflect the relative basicities of the substituents (chlorine and substituted phenyl in the present instance) in the transition state. The present work emphasizes the powerful effect of the α-chloro substituent in this regard; only when the phenyl substituent bears a *p*-nitro substituent can it compete somewhat effectively with this halogen.



In conclusion, a further comment relevant to the results obtained when **14** was treated with excess sulfuryl chloride is in order. Comparison of the direction of initial chlorination in this run (ratio of **15** and **18** to **17** = 1.6:1) with the data when only 1 equiv of chlorinating agent was employed (ratio of **15** to **16** = 1.5:1) indicates that the same directional effect (within experimental error) is operative in both cases as, of course, it should be. Interestingly, however, dichloro sulfide **19** is converted into its S-chlorosulfonium chloride at a more rapid rate than is dichloro sulfide **20**, as indicated by the total conversion of **19** to *p*-nitrobenzyl trichloromethyl sulfide (isolated as its sulfone). Furthermore, the total absence of trichloro sulfones in the run performed with 1 equiv of sulfuryl chloride points to the fact that the reactivity of the various chloro sulfides toward the chlorinating agent is **14** >> **19** > **20**. Since relative rates of chloro sulfonium salt formation very likely represent a quantitative assay of the relative basicities of benzylic sulfides toward the chloronium donor,[7b] the preceding evidence indicates that the same order holds for the basicities of the chloro sulfides in question.



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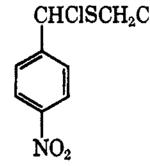

20

Experimental Section[14]

General Procedure for the Preparation of Mercaptans.—A solution of 9.45 g (0.05 mol) of *p*-fluorobenzyl bromide and 4.57 g (0.06 mol) of thiourea in 40 ml of 70% aqueous ethanol was refluxed with stirring for 2 hr and cooled. At this point a small aliquot was isolated and the thiuronium bromide was recrystallized from ethanol to purity, mp 144–145°.

Anal. Calcd for $C_8H_{10}BrFN_2S$: C, 36.23; H, 3.80; N, 10.57. Found: C, 36.19; H, 3.96; N, 10.83.

The remainder of the cold solution was added slowly to a saturated aqueous solution of 16.8 g (0.2 mol) of sodium bicarbonate. The precipitated carbonate salt was separated by filtration and the filtrate was neutralized with hydrochloric acid. After the majority of the carbonate salt had been steam distilled, the neutralized filtrate was added and the steam distillation continued. The liberated mercaptan was extracted with ether; the ether solution was dried and evaporated and the residue was distilled to give 6.32 g (89%) of *p*-fluorobenzyl mercaptan, bp 69° (6 mm).

Anal. Calcd for C_7H_7FS: C, 59.12; H, 4.96; S, 22.55. Found: C, 59.78; H, 4.88; S, 22.59.

From *m*-trifluoromethylbenzyl chloride (Pierce Chemical Co.) there was prepared the thiuronium chloride, mp 194.5–195.5° (from ethanol) and the mercaptan, bp 55° (2.1–2.2 mm), $n^{24}D$ 1.4890. The latter substance was isolated in 72% yield.

Anal. Calcd for $C_9H_{10}ClF_3N_2S$: C, 39.93; H, 3.72; N, 10.35. Found: C, 39.94; H, 3.80; N, 10.45.

Anal. Calcd for $C_8H_7F_3S$: C, 49.99; H, 3.67; S, 16.68. Found: C, 50.30; H, 3.65; S, 16.94.

General Procedure for the Preparation of Benzyl Chloromethyl Sulfides.—Treatment of a solution of 47.6 g (0.30 mol) of *p*-chlorobenzylmercaptan (Wateree Chemical Co.) in 100 ml of dichloromethane with 9.0 g (0.30 mol) of paraformaldehyde and anhydrous hydrogen chloride at −20° under the prescribed conditions gave 43.7 g (70.5%) of **11b**, bp 118–119° (0.4 mm).

Oxidation of a small portion of this material with *m*-chloroperbenzoic acid in chloroform solution[7] gave **13b**, mp 155° (from cyclohexane).

Anal. Calcd for $C_8H_8Cl_2O_2S$: C, 40.18; H, 3.37. Found: C, 40.29; H, 3.48.

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(14) Melting points are corrected and boiling points are uncorrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and by Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer fitted with sodium chloride prisms. The nmr spectra were recorded with a Varian A-60 spectrometer. The mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV.

From *p*-fluorobenzyl mercaptan there was prepared the corresponding chloromethyl sulfide **11a** in 76.5% yield, bp 67° (0.3 mm). The sulfide was likewise characterized as its sulfone **13a**, mp 132° (from cyclohexane).

Anal. Calcd for $C_8H_8ClFO_2S$: C, 43.15; H, 3.62; S, 14.40. Found: C, 43.33; H, 3.69; S, 14.42.

From *m*-trifluoromethylbenzyl mercaptan there was prepared the corresponding chloromethyl sulfide **11c** in 79% yield, bp 67° (0.2 mm). The sulfide was oxidized to its sulfone (**13c**), mp 90° (from cyclohexane), for purposes of characterization.

Anal. Calcd for $C_9H_8ClF_3O_2S$: C, 39.60; H, 2.97; Cl, 31.04. Found: C, 39.64; H, 2.96; Cl, 13.00.

From *p*-nitrobenzyl mercaptan[15] there was prepared the corresponding chloromethyl sulfide **14**, mp 50–51° (from CCl_4), in 70% yield. Oxidation of **14** gave the related sulfone as colorless needles from chloroform–cyclohexane, mp 149.5–150.5°.

Anal. Calcd for $C_8H_8ClNO_4S$; C, 38.48; H, 3.23; Cl, 14.20. Found: C, 38.28; H, 3.16; Cl, 14.02.

General Procedure for the Chlorination and Oxidation of the Benzyl Chloromethyl Sulfides.—Under a nitrogen atmosphere, a solution of 1.0 g (7.3 mmol) of sulfuryl chloride in 10 ml of carbon tetrachloride was added dropwise to a stirred solution of 1.6 g (7.3 mmol) of chloromethyl *p*-nitrobenzyl sulfide (**14**) in 15 ml of the same solvent at 23°. After addition of the sulfuryl chloride had been completed, the solution was refluxed for 2.5 hr and cooled, and the solvent was removed under reduced pressure. The residue was immediately oxidized with 3.1 g (18.2 mmoles) of *m*-chloroperbenzoic acid in cold chloroform. The usual work-up[8] gave a pale yellow oil, the nmr spectrum of which was recorded. Careful chromatography of the oil on 80 g of silica gel [elution with benzene-chloroform (4:1)] afforded **15** and **16** in a ratio of 3:2 (total weight, 1.5 g).

The first compound to be eluted (**15**) was obtained as colorless needles from chloroform–cyclohexane, mp 106.5–107.5°.

Anal. Calcd for $C_8H_7Cl_2NO_4S$: C, 33.82; H, 2.48; Cl, 24.96. Found: C, 33.75; H, 2.37; Cl, 24.83.

The minor component (**16**) was obtained as colorless needles from chloroform-hexane, mp 121–122°.

Anal. Calcd for $C_8H_7Cl_2NO_4S$: C, 33.82; H, 2.48; Cl, 24.96. Found: C, 34.02; H, 2.68; Cl, 24.89.

When **14** (4.34 g, 20 mmol) was treated with 4.05 g (30 mmol) of sulfuryl chloride as above, there was isolated by chromatography on silica gel (in the order of elution) 2.35 g of **17**, mp 162–163° (from chloroform–hexane).

Anal. Calcd for $C_8H_6Cl_3NO_4S$: C, 30.16; H, 1.90; Cl, 33.38. Found: C, 30.23; H, 1.96; Cl, 33.34.

Further elution[16] with benzene–cyclohexane (4:1) gave 250 mg of **18**, mp 110–111° (from chloroform–cyclohexane).

Anal. Calcd for $C_8H_6Cl_3NO_4S$: C, 30.16; H, 1.90; Cl, 33.38. Found: C, 30.38; H, 2.01; Cl, 33.61.

The final compound to be eluted, mp 106.5–107.5°, was found to be **15**, the substance which was eluted first in the previous experiment. Further elution of the column with solvents of increasing polarity gave no additional material.

In similar fashion, reaction of 11.4 g (0.06 mol) of **11a** with 8.8 g (0.065 mol) of sulfuryl chloride afforded a mixture of two sulfones. Chromatography of a weighed aliquot of the total crude product indicated the mixture to be composed of 23% **13a**, mp 132°, and 77% **12a**, mp 62° (from cyclohexane).

Anal. Calcd for $C_8H_7Cl_2FO_2S$: C, 37.54; H, 2.89; S, 12.61. Found: C, 37.37; H, 2.74; S, 12.47.

In like fashion, **11b** afforded a mixture consisting of **13b**, mp 155°, and **12b**, mp 90.5° (from cyclohexane), in a ratio of 4:1.

Anal. Calcd for $C_8H_7Cl_3O_2S$: C, 35.12; H, 2.58; S, 11.72. Found: C, 34.75; H, 2.64; S, 11.71.

When **11c** was treated with sulfuryl chloride and *m*-chloroperbenzoic acid in the above manner, there was isolated upon careful chromatography the chloro sulfones **13c**, mp 90°, and **12c**, mp 70.5° (from cyclohexane), in a ratio of 2:1.

Anal. Calcd for $C_9H_7Cl_2F_3O_2S$: C, 35.19; H, 2.30; Cl, 23.09. Found: C, 35.16; H, 2.32; Cl, 22.96.

In all cases, the ratio of isolated product were found to compare favorably with the integrated intensity ratios of the various proton absorptions in the nmr spectra of the crude oxidation mixtures.

Registry No.—**11a,** 15894-24-3; **11b,** 15894-25-4; **11c,** 15894-26-5; **12a,** 15894-27-6; **12b,** 15894-28-7; **12c,** 15894-29-8; **13a,** 15963-74-3; **13b,** 15893-98-8; **13c,** 15893-96-6; **14** sulfone, 15893-97-7; **15,** 15893-99-9; **16,** 15894-00-5; **17,** 15894-01-6; **18,** 15894-02-7; *p*-fluorobenzyl thiuronium bromide, 15894-03-8; *p*-fluorobenzyl mercaptan, 15894-04-9; *m*-fluorobenzyl thiuronium chloride, 15894-05-0; *m*-fluorobenzyl mercaptan, 15894-06-1; dibenzyl sulfone, 620-32-6; $C_6H_5CH_2SO_2CHCl$-C_6H_5, 6668-15-1; *p*-$NO_2C_6H_4CH_2SO_2CH_2Cl$, 15893-97-7; $C_6H_5CH_2SO_2CHCl_2$, 10038-09-2; $C_6H_5CH_2SO_2CCl_3$, 15894-11-8.

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[15] W. S. Hoffman and E. E. Reid, *J. Amer. Chem. Soc.*, **45**, 1833 (1923); W. J. Horn, *ibid.*, **43**, 2603 (1921).

[16] Clean separation of **17** and **18** was not always achieved. However, fractional recrystallization of the mixed fractions readily yielded pure **17** and **18**.