similar to those described previously[16] and consisted of a Beckman DU monochromator, a four-jet mixing chamber constructed of Hastalloy-C2 with a quartz exit tube serving as absorption cell (0.7 mm i.d.), a photomultiplier (EMI 6256S) with associated power supply, John Fluke Mfg. Co., Model 409A, a Tektronix RM 503 oscilloscope with time base, and a Fairchild camera using Polaroid film. The solutions were pressed through the mixing chamber by a motor-driven syringe drive equipped with magnetic clutch. The mixed solution was taken up in a 50-ml syringe whose barrel activated the time sweep of the scope and disengaged the clutch. Syringes and mixing chamber were jacketed and were kept at 20° by circulating water. The individual runs were carried out by carefully filling the syringes with the solutions of aryldiazomethane and zinc chloride in ether with the concentrations stated in Table IV, care being taken to avoid gas bubbles. The time base of the oscilloscope was chosen to observe the reaction over several half-lives and the results were evaluated from the Polaroid photographs. The results are listed in Table IV.

Infrared monitored runs were carried out on a Beckman IR-7 instrument using a standard Beckman sodium chloride cell. The top exit of the cell was fitted with a Teflon four-jet mixing chamber connected to two syringes which were operated manually. The bottom exit of the cell was connected to another syringe with polyethylene tubing. The flow was stopped manually by clamping the exit tubing. The spectrometer was set at the maximum of the diazo-stretching vibration absorption band (2058 cm^{-1}) and after the flow of the solution had been stopped the decay of this band was monitored by recording a trace on the fast-moving recorder chart. The results listed in Table IV are the average of several runs. In another experiment the region between 2500 and 1700 cm^{-1} was rapidly scanned to detect any band possibly to be associated with an intermediate. None was found.

Continuous-Flow Experiments.—The continuous-flow apparatus consisted of a motor-driven syringe drive equipped with two calibrated syringes connected with polyethylene tubing to a four-jet mixing chamber constructed of Hastalloy C-2. The exit of the mixing chamber was attached to exchangeable capillaries (0.4 cm i.d.) varying in length from 2 to 26 cm. The capillary tip dipped into a flask containing well-stirred cyclohexene. The syringe drive mechanism was equipped with an electrical timer activated by a switch at the beginning of the run and stopped by another switch at the end of the syringe drive. The residence time (τ) of the solution in the capillary was calculated according to $\tau = al/Vt$, where a is the cross section of the capillary, l is its length, V is the total volume delivered during the experiment, and t is the time of the run.

Runs were carried out with phenyldiazomethane and *p*-tolyldiazomethane with zinc chloride in the concentrations stated in Table V. The reaction mixture was then analyzed by calibrated glpc for norcaranes and the yield calculated in a standard manner. The results are listed in Table V.

Isolation of 1-Phenyl-2-ethoxypropane.—The combined reaction mixtures of the stopped-flow experiments with phenyldiazomethane were washed with water and the solvent was evaporated. The residue was extracted with carbon tetrachloride and bromine in carbon tetrachloride was added to a slight excess to precipitate unsaturated products. The solution was filtered and analyzed by glpc on a 5-ft SE-30 column. The major component was trapped in the conventional manner: nmr 7.1 (5) s, 3.2–3.7 (3) m, 2.85 (1) d of d, 2.5 (1) d of d, 1.1 (3) t, 1.08 (3) d. Mass spectrum calcd for $C_{11}H_{16}O^+$: 164.1201. Found: 164.1207.

1-*p*-Tolyl-2-ethoxypropane.—The combined reaction mixtures of the stopped-flow experiments with *p*-tolyldiazomethane were worked up as described above and the product was isolated by glpc on a 5-ft SE-30 column: nmr 7.0 (4) s, 3.15–3.7 (3) m, 2.3–3.0 (2) m, 2.3 (3) s, 1.12 (3) t, 1.05 (3) d. Mass spectrum calcd for $C_{12}H_{18}O^+$: 178.1358. Found: 178.1345.

Registry No.—*sym*-1-Phenyl-2-vinylcyclopropane, 17955-08-7; *anti*-1-phenyl-2-vinylcyclopropane, 17955-09-8; *sym*-7-*p*-anisylnorcarane, 17955-10-1; *anti*-7-*p*-anisylnorcarane, 17955-11-2; *sym*-1-(*p*-anisyl)-2,2,3-trimethylcyclopropane, 17955-12-3; *anti*-1-(*p*-anisyl)-2,2,3-trimethylcyclopropane, 17955-13-4; *sym*-1-(*p*-anisyl)-2-vinylcyclopropane, 17955-14-5; *anti*-1-(*p*-anisyl)-2-vinylcyclopropane, 17955-15-6; *sym*-2-(*p*-anisyl)cyclopropylmethylallyl ether, 17955-16-7; *anti*-2-(*p*-anisyl)-cyclopropyl methylallyl ether, 17955-17-8; 1-(*p*-anisyl)-2,2,3,3-tetramethylcyclopropane, 17953-95-6; 2-(*p*-anisyl)methylenecyclopropane, 17953-96-7; 1-phenyl-2-ethoxypropane, 17953-97-8; 1-*p*-tolyl-2-ethoxypropane, 17953-98-9.

(16) "Technique of Organic Chemistry," Vol. VIII, part II, S. C. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, pp 728–748.

Chlorination of Unsymmetrical Sulfides[1]

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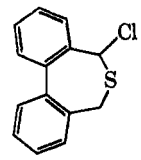
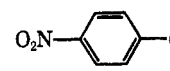
The chlorination of unsymmetrical aliphatic sulfides by N-chlorosuccinimide (NCS) in carbon tetrachloride has been investigated. The resulting mixtures of α-chloro sulfides have been analyzed using nmr spectrometry. The reaction of benzyl *t*-butyl sulfide and benzyl *p*-methoxybenzyl sulfide with sulfuryl chloride results in carbon–sulfur bond cleavage; reaction of these substrates with NCS affords α-chloro sulfides. Ratios of chlorinated products from the reactions of ethyl methyl sulfide with NCS and sulfuryl chloride also indicate significant differences between these chlorinating agents.

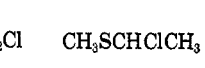
The chlorination of unsymmetrical sulfides has not been studied extensively. Chlorination of benzyl methyl sulfide by sulfuryl chloride[2] or chlorine[3] gives chlorobenzyl methyl sulfide as the only observed product. A powerful directive influence of an α-chloro substituent has also been observed; chlorination of α-chloro sulfides generally leads to exclusive polyhalogenation at one carbon atom.[4] Only two exceptions to this general behavior have been reported. Mixtures of dichloro sulfides are formed in the sulfuryl chloride chlorination of dibenzothiepin **1** and chloromethyl *p*-nitrobenzyl sulfide (**2**).[4d,e] Böhme and Gran isolated



1



2



3

(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955).

(3) H. Böhme and H. J. Gran, *Ann.*, **577**, 68 (1952).

(4) (a) W. E. Truce, G. H. Birum, and E. T. McBee, *J. Amer. Chem. Soc.*, **74**, 3594 (1952); (b) H. Böhme and H. J. Gran, *Ann.*, **581**, 133 (1953); (c) F. Boberg, *ibid.*, **679**, 107 (1964); (d) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4089 (1964); (e) L. A. Paquette, L. S. Wittenbrook, and K. Schreiber, *J. Org. Chem.*, **33**, 1080 (1968).

1-chloroethyl methyl sulfide (**3**) as the only product of the low-temperature chlorination of ethyl methyl sulfide.[3]

The chlorination of unsymmetrical benzylic sulfides by N-chlorosuccinimide (NCS) in carbon tetrachloride has previously been shown to afford mixtures of α-chloro sulfides.[5] Directive effects in these internal competitions are correlated by the Hammett σ–ρ relationship with a ρ of +1.0. This result is consistent with a mechanism which involves abstraction of the more acidic proton from an intermediate chlorosulfonium ion. We have now investigated the chlorination of several unsymmetrical aliphatic sulfides.

Results

Unsymmetrical sulfides were allowed to react with NCS in carbon tetrachloride at 4 ± 1°. The resulting mixtures of α-chloro sulfides were analyzed by integration of appropriate peaks in the 60-Mc nmr spectra of the crude reaction products (see Experimental Section for details for each compound). For example, chlorination of ethyl methyl sulfide affords 1-chloroethyl methyl sulfide (**3**) and chloromethyl ethyl sulfide (**4**). The ratio of the area of the quartet due to the methinyl hydrogen of **3** to that of the singlet due to the chloromethyl protons of **4** is 1.7, indicating that the ratio of the two compounds in the mixture is 3.4.

$$CH_3SCH_2CH_3 + NCS \longrightarrow \underset{\mathbf{3}}{CH_3SCHClCH_3} + \underset{\mathbf{4}}{ClCH_2SCH_2CH_3}$$

Verification of the nmr assignments was achieved by comparison and augmentation of the nmr spectra with authentic samples of the chloro sulfides, which were prepared by the condensation of the appropriate mercaptan and aldehyde in the presence of HCl. The analytical method was verified by the analysis of weighed mixtures of authentic chloro sulfides.

Aliphatic Sulfides.—The results of the chlorination of aliphatic sulfides with NCS are summarized in Scheme I. The site of preferential chlorination is

SCHEME I

$CH_3SCH_2CH_3$ *	$CH_3SCH_2CH_2CH_3$ *	$CH_3SCH(CH_3)_2$ *
5	**6**	**7**
3.4 ± 0.2	3.7 ± 0.1	~10
$CH_3CH_2SCH(CH_3)_2$ *	$CH_3CH_2SCH_2Cl$ *	$(CH_3)_2CHSCH_2Cl$ *
8	**4**	**9**
2.4 ± 0.4	25 ± 3	7.9 ± 0.2
$CH_3CH_2SCH_2CN$ *		$C_6H_5CH_2SCH_2CH_3$ *
10		**11**
		5.6 ± 0.4

denoted by an asterisk. The ratio of the major to the minor component in the chloro sulfide mixture is also indicated. The limits of uncertainty are the deviations for several trials of each reaction. Chlorination of ethylmercaptoacetonitrile (**10**) gave 2-chloro-2-ethylmercaptoacetonitrile as the only product discerned in the nmr spectrum.

Benzyl Isopropyl Sulfides.—Chlorination of the *para*-substituted benzyl isopropyl sulfides **12** afforded mixtures of **13** and **14**. Analyses of these mixtures were made from the nmr spectra of the crude products; the areas of the benzylic protons of **13** and the equivalent methyl groups of **14** were measured. Predominant halogenation was at the benzylic carbon atom (Scheme II). A Hammett treatment of this substituent effect

SCHEME II

$$\underset{\mathbf{12}}{p\text{-}XC_6H_4CH_2SCH(CH_3)_2} + NCS \xrightarrow{CCl_4} \underset{\mathbf{13}}{p\text{-}XC_6H_4CHClSCH(CH_3)_2} + \underset{\mathbf{14}}{p\text{-}XC_6H_4CH_2SCCl(CH_3)_2}$$

a, X = H; **13**/**14** 3.3
b, X = CH_3; **13**/**14** 2.1
c, X = Cl; **13**/**14** 5.9

in terms of the relative reactivities of sulfides **12** at the benzylic position affords a correlation with σ; ρ = +1.1. This is in excellent agreement with the effect of substituents noted in the chlorination of unsymmetrical benzylic sulfides by NCS.[5]

Comparison of NCS and Sulfuryl Chloride.—Benzyl *t*-butyl sulfide (**15**) was allowed to react with NCS in carbon tetrachloride to give the expected chloro sulfide **16**. The chloro sulfide was identified by its nmr spectrum and by conversion into sulfone **17** using *m*-chloroperoxybenzoic acid. Reaction of **15** with sulfuryl chloride did not yield **16**, but instead afforded predominantly *t*-butyl chloride and benzyl disulfide,

$$\underset{\mathbf{15}}{C_6H_5CH_2SC(CH_3)_3} \xrightarrow{NCS} \underset{\mathbf{16}}{C_6H_5CHClSC(CH_3)_3} \longrightarrow \underset{\mathbf{17}}{C_6H_5CHClSO_2C(CH_3)_3}$$

$$\mathbf{15} \xrightarrow{SO_2Cl_2} (CH_3)_3CCl + (C_6H_5CH_2S)_2$$

which were identified by nmr spectral comparison with authentic samples. In a similar way, benzyl *p*-methoxybenzyl sulfide, which has been shown to react with NCS to give a mixture of α-chloro sulfides,[5b] is cleaved by sulfuryl chloride to give *p*-methoxybenzyl chloride, benzyl disulfide, and α-toluenesulfenyl chloride, identified by spectral comparison with authentic samples.

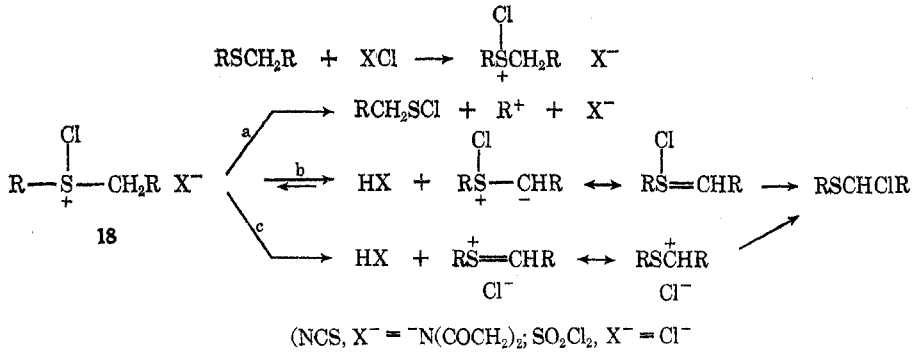
Less dramatic differences in the reactions of NCS and SO_2Cl_2 were noted in the α chlorination of ethyl methyl sulfide. The results of a study in which the reaction temperature was varied are summarized in Table I. The greater selectivity of sulfuryl chloride (favoring the ethyl group) compared with NCS is more prominent at low temperatures. It is noteworthy that the selectivity difference persists in deuteriochloroform, where the NCS reaction is homogeneous. Analysis of weighed samples of authentic chloro sulfides demonstrated that the method of analysis is well within the limits claimed. Unchanged ratios of **3**/**4** in reactions in which ethyl methyl sulfide was allowed to react with an amount of chlorinating agent insufficient for complete halogenation demonstrate that polyhalogenation does not occur to an appreciable extent.

Discussion

A mechanistic pathway which appears to explain these results is presented as Scheme III. The carbon–

(5) (a) D. L. Tuleen and V. C. Marcum, *J. Org. Chem.*, **32**, 204 (1967); (b) D. L. Tuleen, *ibid.*, **32**, 4006 (1967).

SCHEME III
CHLORINATION OF SULFIDES BY NCS AND SO_2Cl_2



(NCS, $X^- = {}^-N(COCH_2)_2$; SO_2Cl_2, $X^- = Cl^-$)

TABLE I
CHLORINATION OF ETHYL METHYL SULFIDE

Solvent	Chlorinating Agent	Temp, °C	Ratio of 3/4
CCl_4	NCS	4 ± 1	3.4 ± 0.2
CCl_4	SO_2Cl_2	4 ± 1	4.9 ± 0.2
$CDCl_3$	NCS	4 ± 1	3.5 ± 0.2
$CDCl_3$	SO_2Cl_2	4 ± 1	4.5 ± 0.3
CCl_4	NCS	25 ± 1	2.8 ± 0.2
CCl_4	SO_2Cl_2	25 ± 1	3.4 ± 0.2
CCl_4	NCS	40 ± 1	2.7 ± 0.2
CCl_4	SO_2Cl_2	40 ± 1	2.8 ± 0.2

sulfur bond cleavage observed in the reactions of benzyl *t*-butyl sulfide and benzyl *p*-methoxybenzyl sulfide with sulfuryl chloride may be readily explained in terms of ionic cleavage of an intermediate chlorosulfonium salt, **18**, where X^- is the chloride ion. Such cleavage (path a) should be facilitated in cases involving the formation of a relatively stable carbonium ion. Cleavage of this type has been previously observed in the sulfuryl chloride chlorination of episulfides,[6] thietane,[2] and *t*-butyl trichloromethyl sulfide,[4a] as well as the NCS chlorination of thietane[7] and in other mechanistically related processes.[8]

We believe that the α chlorination observed in the reactions of NCS with benzyl *t*-butyl sulfide and benzyl *p*-methoxybenzyl sulfide also proceeds through chlorosulfonium salt **18** in which X^- is the succinimidyl anion. Although dissociation constants of succinimide and hydrogen chloride in carbon tetrachloride are not known, it is not unreasonable to assume that hydrogen chloride is the stronger acid; succinimidyl anion would then be a stronger base than chloride ion in carbon tetrachloride. Hydrogen abstraction by the succinimidyl anion at a carbon α to sulfur (paths b or c) would lead to the chloro sulfide products. Competition between paths which lead to cleavage or to hydrogen abstraction logically depends on the basicity of the anion, X^-.

Chlorination of unsymmetrical sulfides by NCS has been previously described as an effective internal competition of hydrogen abstraction at the two α-carbon atoms flanking sulfur in an intermediate chlorosulfonium salt.[5] The positive value of ρ in the Hammett correlation of the results of the chlorination of unsymmetrical benzylic sulfides implicates the relative acidity of the α protons as the determining factor in orientation. This argument (Scheme III, path b) also accounts for the predominant direction of chlorination of sulfides **10**–**12** and the sign of ρ in the chlorination of sulfides **12**.

Consideration of the acidity of the α hydrogens does not, however, explain the directive effects in the chlorination of aliphatic sulfides **5**–**8**. The results for these substrates indicate increasing susceptibility to chlorination of alkyl substituents in the order methyl < ethyl ≈ *n*-propyl < isopropyl. This order would be expected if chlorination proceeded by a free-radical chain mechanism. The direction of preferential halogenation of **4**, **9**, and **10** is opposite to that which would be predicted for a radical chlorination. Other reasons for rejection of a radical mechanism have been summarized elsewhere.[5a] This order would also be expected if the α-carbon atom assumed some carbonium ion character in the transition state for hydrogen abstraction. Path c of Scheme III indicates the concerted removal of a proton and chloride ion from the chlorosulfonium salt. Carbonium ion character is presumably developed at the α carbon in the transition state for this reaction, which generates a carbonium ion. This process is somewhat similar to that proposed by Johnson and Phillips for the reaction of sulfonium salts with methoxide ion.[9]

Paths b and c may be regarded as analogs of the well-known E1cb and E2 mechanisms for 1,2-elimination reactions.[10,11] Path b, in analogy with the E1cb mechanism, should tend to be more important for sulfonium salts involving a reasonably acidic proton α to sulfur, or a more strongly basic abstractor, X^-. If the α hydrogen is not particularly acidic, path c, analogous to the E2 mechanism, may predominate. There presumably exists a continuum of mechanistic possibilities between the two extreme cases.

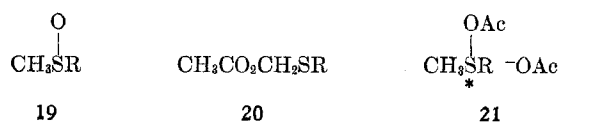
The differences in selectivity observed in the chlorination of ethyl methyl sulfide by NCS and sulfuryl chloride can now be interpreted. Chlorination by sulfuryl chloride involves hydrogen abstraction from the sulfonium salt by chloride ion; the abstractor in the NCS reaction is the more basic succinimidyl anion. The transition state for hydrogen abstraction by chloride ion should lie further along the reaction coordinate than that for abstraction by the succinimidyl anion. In other words, the sulfuryl chloride reaction

(6) G. Y. Epshtein, I. A. Usov, and S. Z. Ivin, *Zh. Obshch. Khim.*, **34**, 1961 (1964).
(7) D. L. Tuleen and T. B. Stephens, *Chem. Ind.* (London), 1555 (1966).
(8) See, for example, G. E. Wilson, Jr., *J. Amer. Chem. Soc.*, **87**, 3785 (1965), and references cited therein.
(9) C. R. Johnson and W. G. Phillips, *J. Org. Chem.*, **32**, 1926 (1967).
(10) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 187 ff.
(11) We do not wish to imply by this comparison any knowledge of the stereochemistry of elimination reactions of chlorosulfonium salts.

more closely resembles path c than does the chlorination by NCS; carbonium ion stability is more important in product determination in the sulfuryl chloride reaction. Therefore, SO_2Cl_2 is more selective (toward the ethyl group) than is NCS in the chlorination of ethyl methyl sulfide.

The powerful directive influence of an α-chloro substituent toward further chlorination at the same carbon atom observed in the chlorination of sulfides **4** and **9** has been previously noted by several investigators.[4] Paquette, Wittenbrook, and Schreiber have explained this effect in terms of inductive electron withdrawal by chlorine, which renders the α hydrogens of the chlorosulfonium salt more acidic.[4e] Conceivably, this directing influence could also reflect the stabilization of an incipient carbonium ion by a resonance interaction involving electron donation from chlorine to carbon.

Johnson, Sharp, and Phillips have recently reported that α-acetoxymethyl sulfides, **20**, are the sole products of the reaction of sulfoxides **19** (R = *n*-propyl, isopropyl, *n*-butyl) with acetic anhydride. This Pummer-type reaction is believed to involve a product-determining hydrogen abstraction from the intermediate acetoxysulfonium salts, **21**. Exclusive hydrogen abstraction at the methyl group is accounted for in terms of the greater acidity of those protons.[12] This directive effect is opposite to that observed in abstractions from the analogous sulfonium salts, **18**. This surprising difference may reflect the differences in basicity of acetate and chloride or succinimidyl anions in inert solvents or the differing abilities of chloride and acetate ions to function as leaving groups.



19 **20** **21**

Experimental Section[13]

Reagents.—N-Chlorosuccinimide was recrystallized from eight times its weight of hot water and dried in air. Sulfuryl chloride (Eastman) was dried and distilled prior to use. Spectrograde carbon tetrachloride, obtained from Matheson Coleman and Bell, was used without further purification.

Sulfides.—Several of the sulfides were commercially available. These were distilled before use. Nmr spectra of all sulfides were consistent with their structure.

Isopropyl methyl sulfide (7) was prepared in 45% yield by the methylation of 2-propanethiol with dimethyl sulfate: bp 85–86°, n^{20}D 1.4364 (lit.[14] bp 84.8°, n^{25}D 1.4362).

Chloromethyl ethyl sulfide (4) was prepared in 50% yield by the method of Böhme[15] from ethanethiol, paraformaldehyde, and HCl in methylene chloride, using anhydrous calcium sulfate to absorb the water produced: bp 58–59° (57 mm); n^{25}D 1.4860 [lit.[15b] bp 50–51° (16 mm); n^{20}D 1.5284]; nmr (CCl_4) 1.32 (triplet, 3 H), 2.75 (quartet, 2 H), and 4.67 ppm (singlet, 2 H).

Chloromethyl isopropyl sulfide (9) was synthesized in 63% yield in a similar manner from paraformaldehyde and 2-propanethiol, using anhydrous magnesium sulfate to absorb water: bp 53–56° (27 mm); n^{25}D 1.4783 [lit.[15b] bp 57–58° (42 mm)].

1-Chloroethyl methyl sulfide (3) was prepared similarly from paraldehyde and methanethiol in 45% yield: bp 50–53° (94 mm); n^{25}D 1.4746 [lit.[15b] bp 51–55° (100 mm)]; nmr (CCl_4) 1.82 (doublet, 3 H), 2.25 (singlet, 3 H), and 5.13 ppm (quartet, 1 H).

Ethylmercaptoacetonitrile (10).—Chloroacetonitrile (7.6 g, 0.1 mol) was added dropwise over 10 min to a solution of sodium ethanethiolate (6.7 g, 0.08 mol) in 70 ml of dimethylformamide. The temperature of the solution rose to 60°. The mixture was stirred at ambient temperature for 6 hr and was poured into 400 ml of water. The product was extracted into ether, washed with water, and dried over magnesium sulfate. Removal of ether and distillation afforded a small amount (1.25 g, 15%) of the desired sulfide: bp 63–64° (4 mm); n^{25}D 1.4731 [lit.[15a] bp 72–73° (13 mm)].

Benzyl ethyl sulfide (11) was prepared from ethyl bromide and sodium α-toluenethiolate in methanol in the normal manner.[16] Distillation afforded material of bp 89–91° (3.5 mm), n^{25}D 1.5488 [lit.[16] bp 98–99° (13 mm)].

Benzyl isopropyl sulfide (12a) was synthesized in 38% yield from 2-bromopropane and sodium α-toluenethiolate in dimethylformamide: bp 90–95° (4–5 mm) [(lit.[16] bp 99–104° (14 mm)].

Isopropyl *p*-methylbenzyl sulfide (12b) was prepared in 86% yield by the reaction of sodium 2-propanethiolate with *p*-methylbenzyl chloride in ethanol, bp 82–84° (1.5 mm), n^{26}D 1.5309.

***p*-Chlorobenzyl isopropyl sulfide (12c)** was prepared analogously in 41% yield from 2-bromopropane and *p*-chlorobenzyl mercaptan in sodium ethoxide: bp 112–115° (3 mm), n^{25}D 1.5501. Oxidation with hydrogen peroxide in acetic acid–acetic anhydride afforded the corresponding sulfone in 82% yield: mp 101–102°; ν_{max} 1130 and 1310 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}ClO_2S$: C, 51.61; H, 5.63. Found: C, 51.39; H, 5.59.

Benzyl *t*-Butyl sulfide (15) was prepared from *t*-butyl mercaptan and α-chlorotoluene in sodium ethoxide. Distillation afforded 83% of the desired sulfide: bp 78–80° (1 mm); n^{26}D 1.5281 [lit.[17] bp 115–116° (15 mm)].

***p*-Methoxybenzyl Chloride.**—Anisole (32.4 g, 0.3 mol), paraformaldehyde (9 g, 0.3 mol), acetic acid (100 ml), concentrated HCl (60 ml), and concentrated H_2SO_4 (5 ml) were mixed and cooled in an ice bath. Gaseous HCl was added at a rate such that the temperature was maintained below 25°. After 20 min, the cooling bath was removed, and HCl addition was continued for 2 hr. The mixture was poured into 400 ml of water, partially neutralized with dilute sodium hydroxide solution, and extracted with ether. The ethereal extract was washed with water, sodium bicarbonate solution, and water and dried over magnesium sulfate. Removal of the ether and distillation afforded a small amount (6 g, 13%) of the desired product, bp 82–85° (1.8–2 mm) [lit.[18] bp 92° (1.5 mm)].

Chlorination of Sulfides by NCS.—The method of chlorination by NCS at 4 ± 1° in carbon tetrachloride is illustrated for ethyl methyl sulfide, **5**. The selectivity ratios in Schemes I and II are based on several chlorinations of each compound. Three, and in some cases, five intergrals were taken on each run and averaged.

Ethyl methyl sulfide (**5**, 0.760 g, 0.01 mol) was dissolved in 6 ml of CCl_4 in a flask containing a thermometer, drying tube and a magnetic stirring bar. NCS (1.348 g, 0.01 mol) was added and the mixture was allowed to stir for 6–7 hr at 4 ± 1° (maintained by an external ice bath). A sample was withdrawn and analyzed by nmr spectrometry. The nmr spectra of the two chloro sulfide products are recorded together with their preparation, earlier in this section. Analysis was made of the chloromethyl singlet of **4** at 4.67 ppm and the methinyl quartet of **3** at 5.13 ppm. Analysis of authentic mixtures of **3** and **4** verified the analytical method.

In Table II are recorded the products of chlorination of sulfides by NCS. Peaks corresponding to the underlined protons were

(12) C. R. Johnson, J. C. Sharp, and W. G. Phillips, *Tetrahedron Lett.*, 5299 (1967).

(13) Melting points were determined with a Thomas–Hoover capillary melting point apparatus and are corrected. Boiling points are uncorrected. Analyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were recorded on a Varian Associates A-60 spectrometer, employing tetramethylsilane as an internal reference. Chemical shifts are reported in parts per million downfield from tetramethylsilane. The nmr spectrometer was purchased with a grant from the National Science Foundation (GP 1683).

(14) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Amer. Chem. Soc.*, **73**, 3627 (1951).

(15) (a) H. Böhme, *Ber.*, **69**, 3, 1610 (1936); (b) H. Bohme, R. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949).

(16) J. Buchi, M. Prost, H. Eichenberger, and R. Lieberherr, *Helv. Chim. Acta*, **35**, 1527 (1952).

(17) H. R. Rheinboldt, F. Mott, and E. Motzkus, *J. Prakt. Chem.*, **134**, 257 (1932).

(18) C. G. Swain and W. P. Langsdorf, Jr., *J. Amer. Chem. Soc.*, **73**, 2813 (1951).

TABLE II

CHLORINATION OF SULFIDES BY N-CHLOROSUCCINIMIDE

	Major product			Minor product		
Sulfide	Structure	Ppm	Mult	Structure	Ppm	Mult
5	$CH_3CHClSCH_3$	5.13	q	$CH_2ClSCH_2CH_3$	4.67	s
6	$CH_3CH_2CHClSCH_3$	4.92	t	$CH_2ClSCH_2CH_2CH_3$	4.68	s
7	$CH_3SCCl(CH_3)_2$	1.90	s	$CH_3CHClSCH(CH_3)_2$	4.73	s
8[a]	$CH_3CH_2SCCl(CH_3)_2$	1.30	t	$CH_3CHClSCH(CH_3)_2$	1.30	d
		1.92	s		1.80	d
4	$CH_3CH_2SCHCl_2$	6.75	s	$CH_3CHClSCH_2Cl$	1.90	d
9	$(CH_3)_2CHSCHCl_2$	6.73	s	$(CH_3)_2CClSCH_2Cl$	2.03	s
11	$C_6H_5CHClSCH_2CH_3$	6.05	s	$C_6H_5CH_2SCHClCH_3$	4.87	q
12a	$C_6H_5CHClSCH(CH_3)_2$	6.13	s	$C_6H_5CH_2SCCl(CH_3)_2$	1.90	s
12b	p-$CH_3C_6H_4CHClSCH(CH_3)_2$	6.05	s	p-$CH_3C_6H_4CH_2SCCl(CH_3)_2$	1.88	s
12c	p-$ClC_6H_4CHClSCH(CH_3)_2$	6.11	s	p-$ClC_6H_4CH_2SCCl(CH_3)_2$	1.90	s

[a] Analysis of the product mixture from this sulfide was made by an indirect method. Let x = amount of major product; y = amount of minor product. The sum of integrals at 1.30 ppm = $3x + 6y$; sum at 1.8–1.92 ppm = $6x + 3y$.

used for the analysis of the mixtures; the chemical shifts and multiplicities of these peaks are indicated in the table.

Chlorination of Benzyl *t*-Butyl Sulfide (15).—Chlorination by NCS in the usual manner afforded *t*-butyl α-chlorobenzyl sulfide, **16**. The nmr spectrum displayed, in addition to aromatic protons, singlets at 1.42 (9 H) and 4.81 ppm (1 H). Distillation afforded material of bp 92–93° (1 mm) contaminated with benzaldehyde (from hydrolysis). Oxidation of **16** with *m*-chloroperoxybenzoic acid by the method of Paquette[4d] gave the sulfone, **17**, 58–61°. Recrystallization from benzene–hexane followed by sublimation gave material of mp 73.5–75°.

Anal. Calcd for $C_{11}H_{15}ClO_2S$: C, 53.54; H, 6.13. Found: C, 53.37; H, 6.11.

Chlorination of **15** by sulfuryl chloride was achieved by slowly adding sulfuryl chloride to a solution of benzyl *t*-butyl sulfide in carbon tetrachloride. Nmr analysis and augmentation showed the major products to be benzyl disulfide and *t*-butyl chloride.

Chlorination of Benzyl *p*-Methoxybenzyl Sulfide.[5b]—Similar reaction of sulfuryl chloride with benzyl *p*-methoxybenzyl sulfide produced *p*-methoxybenzyl chloride, benzyl disulfide, and α-toluenesulfenyl chloride.

Reaction of Sulfuryl Chloride with Ethyl Methyl Sulfide.—The sulfide (1.518 g, 0.02 mol) was dissolved in 8 ml of CCl_4 in a flask fitted with a thermometer, addition funnel, and drying tube. The addition funnel contained a 1-in. layer of Dowex 812 desiccant. Sulfuryl chloride (2.7 g, 0.02 mol) in 7 ml of CCl_4 was added slowly through the addition funnel to the stirred solution of the sulfide, which was cooled in an ice bath. The addition required 90 min. The reaction was allowed to stand for an additional 3–4 hr and was analyzed by nmr. A small quantity of insoluble oily material was formed in the sulfuryl chloride chlorinations in CCl_4. This oil has not been identified; it is insoluble in $CHCl_3$ and soluble in water. It has no apparent effect on the product ratios observed in this study.

Chlorination of ethyl methyl sulfide in $CDCl_3$ and at higher temperatures was performed similarly to methods described for operation at 4 ± 1°. NCS was totally soluble in $CDCl_3$ in the concentrations employed.

Registry No.—**4**, 1708-73-2; **5**, 624-89-5; **6**, 3877-15-4; **7**, 1551-21-9; **8**, 5145-99-3; **9**, 18267-19-1; **11**, 6263-62-3; **12a**, 770-34-3; **12b**, 18267-22-6; **12c**, 18267-23-7.

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