yield, generally displayed a 1:2 molar ratio of 20–50:1 (in one case, 275:1). Dichloroadamantane was formed in 4–8% yield.

Authentic Materials. 1-Chloroadamantane.—The procedure of Stetter,[51] involving 1-adamantanol, gave a 96% yield of product, mp 162.5–163.5° (lit. mp 165°,[21,54] 164.3–165.6°,[51] 164–164.5°,[35,55] 159–160°,[36] 169–170°).[52]

2-Chloroadamantane.—Adamantanone on treatment with excess lithium aluminum hydride produced an 89% yield of crude 2-adamantanol[60,61] which, on contact with phosphorus pentachloride,[62] afforded crude 2-chloroadamantane (>99% yield). Glpc analysis, column A at 160°, showed the purity to be 96%, mp 190–191.8°, lit.[62] mp 186–188° (both in sealed tubes), 192–193.5°.[35]

1,3-Dichloroadamantane.[39]—Adamantane (4.1 g, 0.03 mol) on exposure to aluminum chloride (4 g, 0.03 mol) at room temperature in carbon tetrachloride (60 ml) for 4 hr produced 1,3-dichloroadamantane in low yield. When half of the carbon tetrachloride was replaced with methylene chloride, after 10 min 1,3-dichloroadamantane was obtained in 49% yield, mp 131–131.5° (lit. mp 133°,[63] 132–134°,[64] 129.5–131.5°),[52] in addition to an appreciable amount of chloroadamantane.

(60) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961).

(61) E. L. Eliel, R. J. L. Martin, and D. Nasipuri, *Org. Syn.*, **47**, 16 (1967).

(62) W. Hoek, J. Strating, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **85**, 1045 (1966).

(63) H. Stetter and C. Wulff, German Patent 1,101,410 (1960); *Chem. Abstr.*, **56**, 14119 (1962).

(64) F. N. Stepanov and Yu I. Srebrodol'skii, *Vestn. Kiev Politekh. Inst., Ser. Khim.-Tekhnol.*, **2**, 6 (1967); *Chem. Abstr.*, **67**, 32355 (1967).

1-(1,2-Dichloro-4-phenyl)adamantane.—1-Bromadamantane (6.45 g, 0.03 mol) and ferric chloride (1.8 g, 0.011 mol) in *o*-dichlorobenzene (60 ml) at 78–82° for 1.6 hr gave dark brown, crude product which, on two crystallizations from benzene, gave white crystals, 3.75 g (44% yield), mp 115–115.3°. The infrared spectrum was essentially identical with the infrared spectrum of the product from adamantane–ferric chloride–*o*-dichlorobenzene.

When half of the *o*-dichlorobenzene was replaced by carbon tetrachloride, the reaction yielded the same aromatic product, along with chloroform, identified by glpc peak enhancement with columns C and D.

Registry No.—Adamantane, 281-23-2; ferric chloride, 7705-08-0; 1-chloroadamantane, 935-56-8; 2-chloroadamantane, 7346-41-0; *o*-dichlorobenzene, 95-50-1; antimony pentachloride, 7646-18-9.

Acknowledgment.—Our appreciation is expressed to the Graduate School of the University of Wisconsin-Milwaukee for support of this work. We thank Dr. George A. Olah for making available unpublished data, and Dr. Kurt W. Field for his general helpfulness. Dr. J. L. M. A. Schlatmann supplied a sample of 2-chloroadamantane for which we are grateful.

Synthesis of α,α-Dichlorosulfenyl Chlorides

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A general synthesis of stable α,α-dichlorosulfenyl chlorides from *S*-benzyl sulfides containing an active methylene group is presented. The mechanism of these chlorination reactions is discussed.

The synthesis of aryl sulfenyl halides by the treatment of certain aryl benzyl sulfides with sulfuryl chloride has been reported by Kharasch and Langford.[1] In this connection we wish to report a general facile

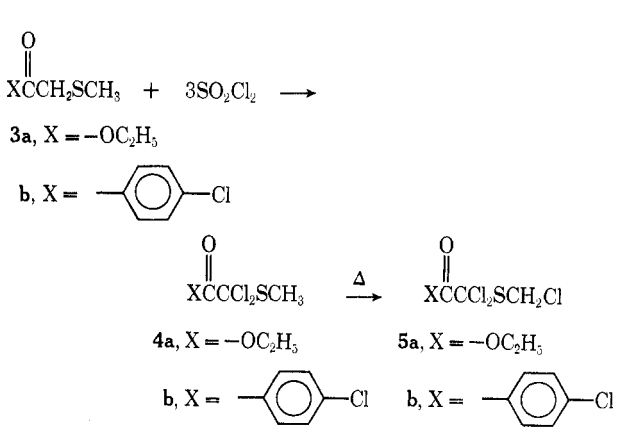
$$ArSCH_2C_6H_5 \longrightarrow ArSCl + C_6H_5CH_2Cl$$

synthesis of stable, novel α, α-dichlorosulfenyl chlorides by the action of sulfuryl chloride on *S*-benzyl sulfides containing an active methylene group.

The general reaction for the synthesis of α,α-dichlorosulfenyl chlorides from β-keto sulfides is depicted in Scheme I.

As can be seen in Table I, several α-carbamoyl *S*-benzyl sulfides gave dichlorosulfenyl chlorides in good yield. Chlorine was an adequate substitute for sulfuryl chloride. The products here were easily obtained in a pure state and were stable pale yellow to white solids. They were characterized by their elemental analysis and nmr spectra. Their nmr spectra are interesting in that they suggest a large barrier to rotation around the N–C bond; **2d** shows two septets for the methine protons separated by 1.4 ppm. Thus the carbonyl oxygen would be expected to be somewhat nucleophilic.

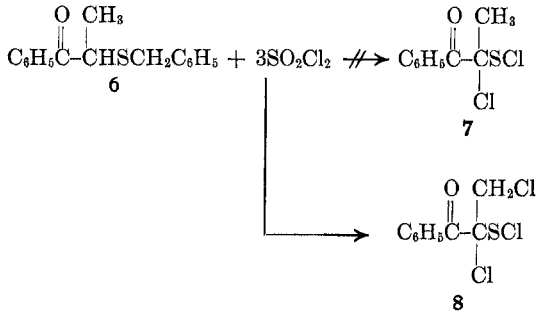
The preparation of α,α-dichlorosulfenyl halides is general in that **1g**, **1h**, and **1i** are also satisfactory. Unlike the α-carbamoyl sulfides, refluxing of these sulfides in neat sulfuryl chloride was desirable to effect the cleavage. Also, unlike the α-carbamoyl sulfides, only *S*-benzyl sulfides were satisfactory; the *S*-methyl sulfides did not cleave but preferred to undergo further chlorination. Thus it appears that, if an SCH_3 group is employed, an amide function is necessary for the cleavage.



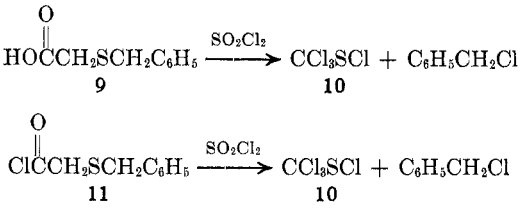
An α-chlorosulfenyl chloride is also formed when an aliphatic substituent is placed α to the carbonyl as in **6**. The expected product, **7**, was not formed but a high yield of **8** was obtained. Here the methyl group is monochlorinated in a unique β chlorination.

The β-carboxyl *S*-benzyl sulfides did not yield the expected α,α-dichlorosulfenyl chloride. When **9** was chlorinated the products were trichloromethylsulfenyl

(1) N. Kharasch and R. B. Langford, *J. Org. Chem.*, **28**, 1903 (1963).

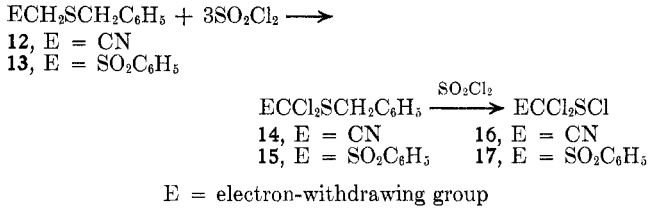


chloride (**10**) and benzyl chloride. Likewise, chlorination of **11** also gave trichloromethylsulfenyl chloride



and benzyl chloride. Here it is possible that only one pathway is involved, since **9** may give **11** under the reaction conditions.

In order to further define the scope of the synthesis of α,α-dichlorosulfenyl chlorides, two sulfides containing no carbonyl function were prepared. Upon treatment with sulfuryl chloride at room temperature these

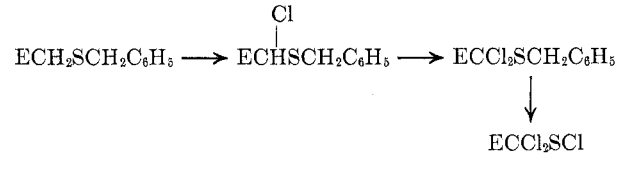


E = electron-withdrawing group

two sulfides gave the corresponding dichlorosulfide. However, upon heating with additional sulfuryl chloride **14** and **15** were converted to their respective α,α-dichlorosulfenyl chlorides.

Considering the above results one can conclude that the synthesis of α,α-dichlorosulfenyl chlorides from *S*-benzyl sulfides containing an active methylene group is general in that a variety of electron-withdrawing groups may be employed.

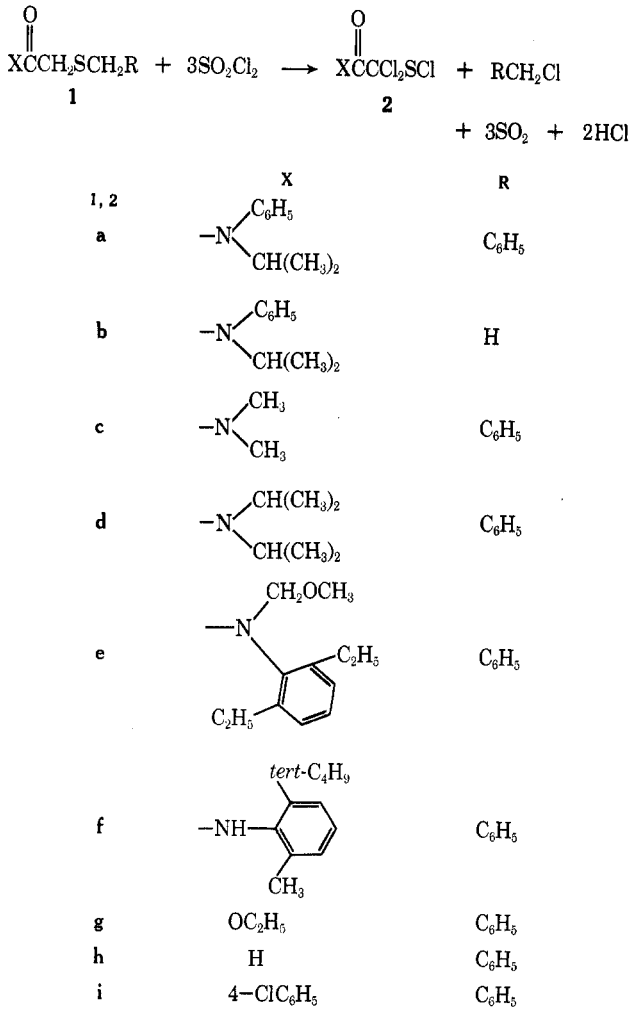
Mechanism of Chlorination.—The sequence of reactions leading to the α,α-dichlorosulfenyl chlorides seemingly involves monochlorination followed by dichlorination and finally cleavage. When **1a** is treated



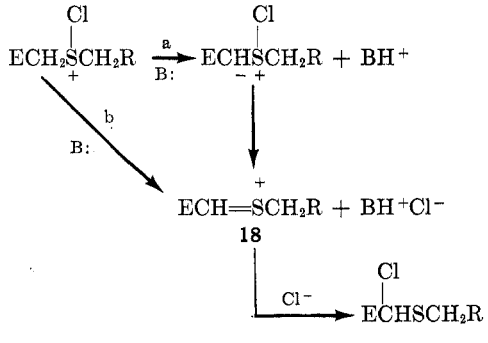
with only 1 equiv of sulfuryl chloride the monochlorosulfide is formed in high yield.[2] Treatment of **12** and **13** with excess sulfuryl chloride at room temperature led to their respective dichlorosulfides, which were converted to sulfenyl chlorides upon heating with sulfuryl chloride.

(2) That the chlorine resided next to the carbonyl was determined unambiguously by acid hydrolysis of the monochlorosulfide to *N*-isopropyl *N*-phenylglyoxyamide.

SCHEME I



The two most likely possibilities for the mechanism of the chlorination are shown below. Pathway a represents an E1cB elimination of hydrogen chloride from the chlorosulfonium salt, while pathway b depicts an



E2 elimination. When **1a** was chlorinated in the presence of 2 equiv of deuteriomethanol the α-chlorosulfide produced contained less than 5% deuterium as shown by nmr and mass spectrograph studies. Thus one can conclude that if the ylide is formed it is not formed reversibly.[3]

It is interesting to note that the chlorine always migrates to the side of the sulfur containing the electron-

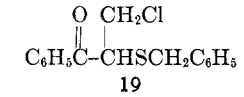
(3) G. E. Wilson in a recent paper has concluded that benzyl sulfide is chlorinated *via* an E2 mechanism on the basis of kinetic isotope effects and the nonobservance of deuterium in the product, monochlorobenzyl sulfide, when benzyl sulfide is chlorinated in the presence of deuterium chloride. See G. E. Wilson and M. G. Huang, *J. Org. Chem.*, **35**, 3002 (1970).

TABLE I
α,α-DICHLOROSULFENYL CHLORIDES

Compd	Empirical formula	Yield, %	Mp, °C, or bp, °C (mm)	Element	Calcd, %	Found, %	Comments
2a	$C_{11}H_{12}Cl_3NOS$	68	121–122	C	42.26	42.33	
				H	3.87	3.89	
				N	4.48	4.66	
2c	$C_4H_6Cl_3NOS$	37	47–48	Cl	47.80	48.01	
2d	$C_8H_{14}Cl_3NOS$	65	121–134	C	34.48	34.62	
				H	5.06	5.10	
2e	$C_{14}H_{18}Cl_3NO_2S$	65	63–65	C	45.36	45.39	
				H	4.89	4.89	
				Cl	28.67	28.76	
2f	$C_{13}H_{16}Cl_3NOS$	76	196–198	C	45.83	46.02	
				H	4.73	4.90	
				Cl	35.22	35.50	
2g	$C_4H_5Cl_3O_2S$	34	81–82 (10)	C	21.49	21.70	
				H	2.25	2.31	
				Cl	47.59	47.31	
2h	C_2HCl_3CO		61–62 (20)				Characterized by its mass spectrum (94% pure by vpc)
2i	$C_8H_4Cl_4OS$	65	27–28	C	33.13	33.28	
				H	1.39	1.36	
				Cl	48.90	48.67	
8	$C_9H_7Cl_3OS$	10	35–43	C	40.10	40.35	
				H	2.62	2.51	
				Cl	39.46	39.26	
16	C_2Cl_3NS	10	65–66 (25)				Characterized by its mass spectrum (100% pure by vpc)
17	$C_7H_5Cl_3O_2S_2$	77	62–64	C	28.83	29.03	
				H	1.71	1.67	
				Cl	36.48	36.63	

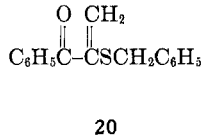
withdrawing group. Thus proton removal is the product-determining step in these chlorinations. This is in agreement with the findings of Tuleen,[4] who postulated that, in the chlorination of unsymmetric benzylic sulfides, the relative acidity of the α protons is the predominant factor in orientation when a reasonably acidic proton is involved. They also suggest[4] that, when the proton is not reasonably acidic, the orientation is determined by the stability of the sulfonium ion (**18**) formed.

The sequence of reactions leading to **8** is somewhat surprising. When **6** was treated with 1 equiv of sulfuryl chloride the β-chlorosulfide (**19**) rather than the



19

α-chlorosulfide was formed in high yield. Three possibilities for the mechanism of this chlorination are (1) elimination of hydrogen chloride from the intermediate chlorosulfonium salt to give acrylphenone and benzyl sulfenyl chloride[5] which can recombine to give **19**, (2) elimination of hydrogen chloride from the intermediate chlorosulfonium salt to give a sulfonium ion analogous to **18** which can lose a proton to give **20** (addition of hydrogen chloride to **20** would give **19**), and (3) the α-chlorosulfide **21** could rearrange to **19** *via*



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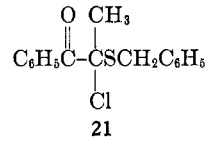
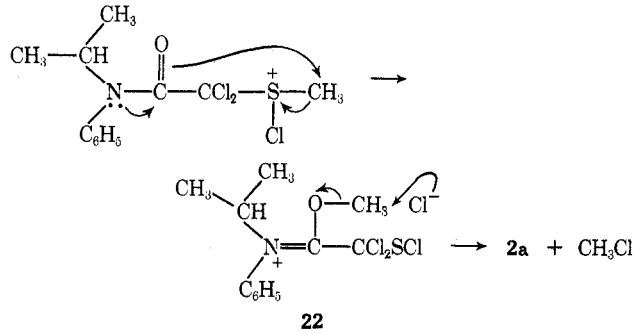


21

20. No distinction between these mechanisms has been made.

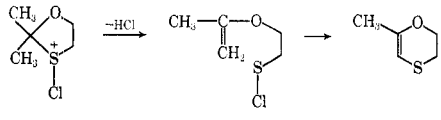
Since chlorination of **3a** and **3b** does not yield sulfenyl chlorides and chlorination of **1b** does give a sulfenyl chloride and methyl chloride, it is tempting to conclude that the nucleophilic carbonyl oxygen is involved in the cleavage of **1b**.[6] One explanation involves neighboring-group participation which results in a five-membered cyclic transition state which subsequently gives **22**.



22

(4) P. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969).

(5) G. E. Wilson has suggested that the chlorination of 2,2-dimethyl-1,3-oxathiolone, which gives 2-methyl-1,4-oxathiene, proceeds *via* a similar



cleavage–recombination sequence. See G. E. Wilson, Jr., *J. Amer. Chem. Soc.*, **87**, 3786 (1965).

(6) S. Winstein and R. Baschan have determined that amide oxygens are more reactive neighboring groups than ester oxygens. See S. Winstein and R. Baschan, *ibid.*, **72**, 4669 (1950).

This intermediate presumably yields the sulfenyl chloride. However, such nucleophilic substitutions make a large demand on the nucleophile and leaving groups to line up in the transition state.

An alternative explanation involves a similar intermolecular process. This mechanism suggests that **3b** can be made to go to the sulfenyl chloride in the presence of **2a**. When this experiment was carried out no cleavage was detected. It should be noted, however, that this result does not rule out an intermolecular process for the cleavage of **1b**. Further studies concerning these α,α-dichlorosulfenyl chlorides are in progress and will be reported in a later paper.

Experimental Section

General.—The mass spectra were determined with a Perkin-Elmer 720 double-focusing mass spectrometer. Melting points were determined with a Mel-Temp apparatus and are uncorrected. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian A-60 spectrometer. The sulfides employed, with the exception of that listed below, were synthesized by routine alkylation of sodium thiolates with the appropriate halide. Analysis were performed by Galbraith Laboratories or Atlantic Microlab.

General Procedure for the Preparation of α,α-Dichlorosulfenyl Chlorides.—To 0.1 mol of the appropriate benzyl sulfide in *ca.* 200 ml of CH_2Cl_2 at 0° was added dropwise 0.3 mol of sulfuryl chloride. After the addition was completed, the flask was allowed to warm to room temperature and stir for *ca.* 1 hr additional. Removal of the solvent gave the crude product mixture. In instances when an α-carbamoyl methyl sulfide was not used, it was desirable to add 50 ml of additional sulfuryl chloride followed by *ca.* 30 min of refluxing. Then the excess sulfuryl chloride was stripped off. The benzyl chloride could be removed by recrystallizing the product from petroleum ether (bp 30–75°) or, in the case of liquids, careful spinning-band distillations (See Table I). The benzyl chloride was confirmed in all instances by spiking the crude product with authentic benzyl chloride and noting that no additional peaks appeared. Also, in several cases, benzyl chloride was identified by comparing its ir spectrum to that of authentic material and by its mass spectrum.

Treatment of Benzyl *N*-Isopropyl-*N*-phenylcarbamoylmethyl Sulfide with Chlorine.—Chlorine was bubbled through 5 g (0.18 mol) of **1a** in 100 ml of methylene chloride for 1 hr. The solvent was removed and the resulting solid was washed with pentane. The yield of α,α-dichloro-α-(*N*-phenyl-*N*-isopropylcarbamoyl)methyl sulfenyl chloride was 81%, mp 123–124°. The melting point of authentic **2a** is 121–122°. This material was identical with that prepared by chlorination of **1a** (see Table I).

α-Benzylthiomethyl Phenyl Sulfone.—To 15.7 g (0.083 mol) of α-chloromethyl phenyl sulfone in 50 ml of DMF was added 2.0 g of 56.2% sodium hydride in mineral oil (exothermic) followed by 10.3 g (0.083 mol) of benzylthiol. After refluxing overnight, *ca.* 250 ml of water was added followed by extraction with methylene chloride. Removal of solvent gave a slurry which solidified upon addition of ether: yield 8.5 g (37%); mp 105–107°; nmr ($CDCl_3$) τ 2.3 (Ar, m), 6.0 (CH_2, s), 6.2 (CH_2, s).

Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07. Found: C, 60.49; H, 5.12.

Preparation of α,α-Dichloro-α-cyanomethyl Benzyl Sulfide.—The general procedure for chlorination of sulfides at 0° was followed. The oil was purified by low-temperature recrystallization from petroleum ether, yield 95%.

Anal. Calcd for $C_9H_7Cl_2NS$: C, 46.57; H, 3.04. Found: C, 46.60; H, 3.09.

α,α-Dichloro-α-phenylsulfonylmethyl Benzyl Sulfide.—To 7.0 g (0.025 mol) of **13** in *ca.* 200 ml of methylene chloride at 0° was dropped in 10.1 g (0.075 mol) of sulfuryl chloride. After stirring for 1 hr, the solvent was removed to give 7.1 g of an oil which solidified upon scratching, mp 66–75°. The product was recrystallized from ether: mp 83.5–84.5°; nmr ($CDCl_3$) τ 1.8–2.7 (m, 10 H), 5.5 (m, 2 H).

Anal. Calcd for $C_{14}H_{12}Cl_2O_2S_2$: C, 48.42; H, 3.48; Cl, 20.42. Found: C, 48.46; H, 3.50; Cl, 20.39.

Chlorination of α-Benzylthioacetic Acid.—To 18.2 g (0.10 mol) of α-benzylthioacetic acid in methylene chloride at 0° was slowly added 39 g (0.3 mol) of sulfuryl chloride. After warming to room temperature and stirring for 2 additional hr, nmr indicated no benzyl chloride formation. To this neat oil was added 50 ml of additional sulfuryl chloride followed by refluxing for 30 min. After the excess sulfuryl chloride was stripped off, spinning-band distillation at 65–65.5° (20 mm) gave pure trichloromethylsulfenyl chloride. The major peaks in the mass spectrum were as follows: *m/e* 184 (M^+), 149 ($M^+ - Cl$), 114 ($M^+ - 2Cl$), and 117 (CCl_3^+). The residue from the distillation was shown to be benzyl chloride by nmr: τ 5.5 (2 H), 2.6 (5 H). Addition of authentic benzyl chloride failed to produce a new peak.

Chlorination of α-Benzylthioacetyl Chloride.—This procedure was identical with that for α-benzylthioacetic acid. Spinning-band distillation at 65–66° (20 mm) gave pure trichloromethylsulfenyl chloride whose ir was identical with that of authentic trichloromethylsulfenyl chloride. The residue from the distillation was shown to be benzyl chloride by nmr: τ 5.5 (2 H), 2.6 (5 H). Addition of authentic benzyl chloride failed to produce a new peak.

Chlorination of α-(*N*-Phenyl-*N*-isopropylcarbamoyl)methyl Methyl Sulfide.—To 15.6 g (0.067 mol) of **1b** in 100 ml of methylene chloride at 0° was slowly added 23 g (0.21 mol) of sulfuryl chloride. After stirring for 15 min, the solvent was removed and a solid remained which was washed with petroleum ether, yield 17 g (82%), mp 119–121° (ether). The nmr and melting point were the same as that for authentic **2a** mentioned in Table I. In order to identify the other product, the reaction was repeated employing ethylene dichloride as the solvent. Nitrogen was passed over the reaction into a Dry Ice trap in order to trap the volatile products. Examination of the nmr of the volatile products showed a peak at τ 6.25 (SO_2) from ethylene chloride and a peak at τ 7.0 (SO_2) from methyl chloride [lit.[7] τ 6.9 (CCl_4)]. The mass spectrum of the mixture confirmed the presence of methyl chloride: *m/e* 50 (M^+), 15 (CH_3^+). At no time could methylene dichloride be detected as a reaction product. Removal of the ethylene dichloride from the reaction mixture gave **2a**, mp 119–121°. The mixture melting point with authentic material was undepressed.

Chlorination of α-Carbethoxymethyl Methyl Sulfide.—To 8.5 g (0.0635 mol) of **3a** in methylene chloride at 0° was added 27 g of sulfuryl chloride. The solvent was removed after stirring for 1 hr at room temperature. The nmr of the liquid suggested that the α-methylene was chlorinated: τ 5.5 (q, 2 H), 7.5 (s, 3 H), 8.5 (5, 3 H). To this liquid was added 10 g of additional sulfuryl chloride followed by refluxing for 30 min. The excess sulfuryl chloride was stripped off and the product, **5a**, was distilled: bp 120–122° (5 mm); yield 14.2 g [0.060 mol (95%)]; nmr ($CDCl_3$) τ 4.9 (CH_2, s), 5.5 (CH_2, q), 8.5 (CH_3, t).

Anal. Calcd for $C_5H_7Cl_3O_2S$: C, 25.28; H, 2.97. Found: C, 25.27; H, 3.12.

Chlorination of α-(4-Chlorophenacyl)methyl Methyl Sulfide.—To 10.0 g (0.05 mol) of **3b** in methylene chloride at 0° was slowly added 21 g (0.15 mol) of sulfuryl chloride. After 15 min, the solvent was removed to yield 11.6 g (86%) of pure **4b**: nmr ($CDCl_3$) τ 2.2 (Ar, q), 7.5 (CH_3, s).

Anal. Calcd for $C_9H_7Cl_3OS$: C, 40.10: H, 2.62. Found: C, 40.01; H, 2.82.

Heating of **4b** with additional sulfuryl chloride at reflux for 15 min gave an oil after the excess sulfuryl chloride was removed. The nmr suggested the product to be **5b**: τ 2.1 (q, 4 H), 5.0 (s, 1.5 H).

Benzyl α-Chloromethyl-α-phenacylmethyl Sulfide.—To 25.6 g (0.10 mol) of benzyl α-methyl-α-phenacylmethyl sulfide in methylene chloride at 0° was slowly added 13.4 g (0.10 mol) of sulfuryl chloride. After warming to room temperature and stirring for 1 hr, the solvent was removed. Some of the oil could be crystallized by cooling in Dry Ice under pentane: yield 17 g (60%); mp 48–51° (from pentane); nmr ($CDCl_3$) τ 2.1–2.9 (m, aromatic), 5.3–6.4 (m, $CHCH_2$), 6.3 (s, SCH_2). The nmr of the crude oil was the same as that of the purified solid.

Anal. Calcd for $C_{16}H_{15}ClOS$: C, 66.08; H, 5.20. Found: C, 66.20; H, 5.35.

Chlorination of α-(*N*-Phenyl-*N*-isopropylcarbamoyl)methyl Benzyl Sulfide.—To a methylene chloride solution of 11.6 g (0.04 mol) of **1a** at 0° was added 5.36 g (0.04 mol) of sulfuryl

(7) A. L. Allred and E. G. Rochow, *ibid.*, **79**, 5361 (1957).

chloride. After 30 min, the solvent was removed and a solid remained, mp 86–87°. The nmr was consistent with α-(*N*-phenyl-*N*-methylcarbamoyl)-α-chloromethyl benzyl sulfide: a multiplet at τ 2.9 (aromatic), a heptet at τ 5.2 ($CHMe_2$), a singlet at τ 5.2 (CHCl), a singlet at τ 6.1 (CH_2), and a doublet at τ 9.0 [$CH(CH_3)_2$]. The yield was 86%.

Anal. Calcd for $C_{18}H_{20}ClNOS$: C, 64.75; H, 6.04; N, 4.20. Found: C, 64.86; H, 5.91; N, 4.21.

In order to ensure that the chlorine was assigned to the correct position, it was hydrolyzed by acidic 2,4-DNP reagent. A solid formed which was recrystallized from ethanol, mp 192–192.5°. Its elemental analysis was consistent with the DNP derivative of *N*-phenyl-*N*-isopropyl glyoxyamide.

Anal. Calcd for $C_{17}H_{17}N_5O_5$: C, 54.98; H, 4.61; N, 18.86. Found: C, 54.73; H, 4.68; N, 18.64.

The reaction was repeated with 2 equiv of deuteriomethanol added before the addition of sulfuryl chloride. The nmr of the product was identical with that shown above. The mass spectrum of the product indicated less than 5% deuterium incorporation in the highest mass found, *m/e* 265. This fragment is apparently a result of a Ramberg–Bachlund type rearrangement.

Chlorination of a Mixture of α-(*N*-Phenyl-*N*-isopropylcarbamoyl)-α,α-dichloromethylsulfenyl Chloride and *p*-Chlorophenacyl-α,α-dichloromethylsulfenyl Chloride.—To a mixture of 7.5 g (0.025 mol) of **2a** and 5.0 g (0.025 mol) of **3b** in *ca.* 100 ml of ethylene dichloride was dropped in 10 g (0.075 mol) of sulfuryl chloride. At the end of the addition, the nmr of the reaction mixture showed a SCH_3 (τ 7.5) and no methyl chloride. At the end of 2 days the SCH_3 peak was nearly gone but a SCH_2Cl peak (τ 5.0) had appeared. The integration showed nearly a quantitative conversion to **5b**.

Registry No.—**2a**, 31328-46-8; **2c**, 31328-47-9; **2d**, 31328-48-0; **2e**, 31328-49-1; **2f**, 31328-50-4; **2g**, 31428-86-1; **2h**, 31328-51-5; **2i**, 31328-52-6; **4b**, 31428-87-2; **5a**, 31328-53-7; **8**, 31385-53-2; **16**, 31328-54-8; **17**, 31385-54-3; **19**, 31328-55-9; α-benzylthiomethyl phenyl sulfone, 31328-56-0; α,α-dichloro-α-phenylsulfonylmethyl benzyl sulfide, 31328-57-1; α-(*N*-phenyl-*N*-methylcarbamoyl)-α-chloromethyl benzyl sulfide, 31328-58-2; *N*-phenyl-*N*-isopropyl glyoxyamide 2,4-DNP, 31328-59-3.

An Ultraviolet Spectroscopy Study on Sulfonium Salts and on an Interaction between Sulfonium Salts and Molecular Oxygen

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The ultraviolet absorption spectra of various trialkyl-, alkyldiaryl-, and triarylsulfonium salts were measured in a nitrogen atmosphere and in an oxygen atmosphere at −40 ± 1 to 25 ± 1°. A high intensity band near 200 mμ was found in these spectra and assigned to be a transition of nonbonding $3p_z$ lone-pair electon of the central sulfur to a vacant 3d sulfur orbital [$(3p_z)^2 \rightarrow (3p_z)(3d)$]. The calculation by the use of ASMO–SCF method well explained this transition band. Solvents used for these measurements exhibited a noticeable effect on the excitation energy of the transition. In a nitrogen atmosphere, nonpolar solvents allowed the transition at longer wavelengths than polar ones. This solvent effect may closely relate to the nature of 3d sulfur orbitals caused by the interaction with the solvents. In an oxygen atmosphere, this band shifted to longer wavelengths in the order of 0.05–0.25 eV. This red shift caused by oxygen increased with the decrease in the dielectric constants of the solvents. Finally, the interaction between the sulfonium salt and molecular oxygen was briefly discussed in connection with the red shift caused by oxygen.

Many chemical studies on the ultraviolet absorption spectra of various sulfur compounds have been made[2–6] with particular reference to the d–π conjugation. Notwithstanding these studies of the ultraviolet spectra, particularly of sulfides,[2–8] sulfones,[2,4,9–12] sulfoxides,[4,12–15] and sulfonium salts,[14–18] the absorption band attributed to the excitation of sulfur atom has not been clarified satisfactorily as yet because of a lack of sufficient knowledge about the bond nature of these sulfur compounds and the shell expansion of their d orbitals. In connection with our previous studies[19–22] on the catalytic properties of sulfonium compounds in the liquid phase hydrocarbon oxidation, it was required necessarily to study the ultraviolet spectra of sulfonium salts and those in the presence of molecular oxygen.

Concerning the latter, ultraviolet spectroscopic studies of the interaction between organic compounds and molecular oxygen have been recently developed by Evans,[23] Munck and Scott,[24] and Tsubomura, *et al.*[25,26] These studies have been based on the charge-transfer theory of Mulliken,[27–30] namely, on "contact

(1) Faculty of Engineering, Kumamoto University, Kurokami-machi, Kumamoto, Japan.

(2) (a) M. Mohler and J. Sorge, *Helv. Chim. Acta*, **23**, 1200 (1940); (b) K. Bowden, E. A. Braude, and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

(3) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **71**, 84, 231 (1949).

(4) H. H. Szmant and J. J. McIntosh, *ibid.*, **73**, 4356 (1951).

(5) H. P. Koch, *J. Chem. Soc.*, 387, 408 (1949).

(6) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, N. Y., 1951.

(7) A. Mangini and R. Passerini, *J. Chem. Soc.*, 1168 (1952).

(8) A. Mangini, *J. Chim. Phys. Physicochim. Biol.*, 240 (1959).

(9) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **72**, 1292 (1950).

(10) H. P. Koch, *J. Chem. Soc.*, 408 (1949).

(11) G. Leandri, A. Mangini, and R. Passerini, *ibid.*, 1386 (1957).

(12) G. Leandri, A. Mangini, and R. Passerini, *Gazz. Chim. Ital.*, **84**, 73 (1954).

(13) H. P. Koch, *J. Chem. Soc.*, 2892 (1950).

(14) S. Oae and C. Zalt, *J. Amer. Chem. Soc.*, **82**, 4938, 5359 (1960).

(15) F. G. Bordwell and P. J. Boutan, *ibid.*, **79**, 717 (1957).

(16) D. C. Nicholson, E. Rothstein, R. W. Saville, and R. Whiteley, *J. Chem. Soc.*, 4019 (1953).

(17) S. Oae and C. C. Price, *J. Amer. Chem. Soc.*, **80**, 3425 (1958).

(18) E. Rothstein, *J. Chem. Soc.*, 3991 (1953).

(19) K. Fukui, K. Ohkubo, and T. Yamabe, *Bull. Chem. Soc. Jap.*, **42**, 312 (1969).

(20) K. Ohkubo, T. Yamabe, and K. Fukui, *ibid.*, **42**, 1800 (1969).

(21) K. Ohkubo, T. Yamabe, and K. Fukui, *ibid.*, **42**, 2220 (1969).

(22) K. Ohkubo, T. Yamabe, and K. Fukui, *ibid.*, **43**, 1 (1970).

(23) D. F. Evans, *J. Chem. Soc.*, 345 (1953); 1351, 3885 (1957); 2753 (1959); *Proc. Roy. Soc., Ser. A*, **255**, 55 (1960).

(24) A. U. Munck and J. F. Scott, *Nature*, **177**, 587 (1956).

(25) H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960).

(26) H. Ishida, H. Takahashi, H. Sato, and H. Tsubomura, *ibid.*, **92**, 275 (1970).

(27) R. S. Mulliken, *J. Chem. Phys.*, **7**, 14, 20 (1939).

(28) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

(29) R. S. Mulliken, *J. Phys. Chem.*, **56**, 811 (1952).

(30) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).