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The Reaction of Sulfenyl Chlorides with Thioethers. I. The Scope of the Reactions

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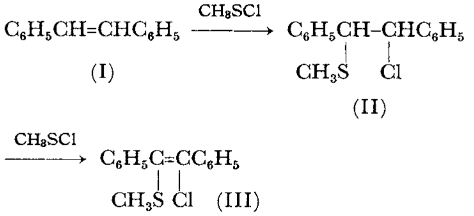
It was found that thioethers reacted with sulfenyl chlorides to give four kinds of products. When the alkyl part of the thioether is capable of producing a rather stable carbonium ion, the thioether gives the chloride and an olefin, which are derived from the cation, the latter reacting also with the sulfenyl chloride to give adducts. There is another path to afford alkyl chloride; that is, an S_N2-type reaction takes place when the alkyl part gives a less stable carbonium ion. The third and fourth products are α-chloro sulfide and α,β-unsaturated sulfide, which are seemingly produced *via* a common intermediate. The latter may react further with the sulfenyl chloride to give enedithiol derivatives.

During the course of other investigations in this laboratory, a rather unexpected reaction was encountered.[1] Namely, when stilbene (I) and an excess of methanesulfenyl chloride were allowed to react, the product was not the one expected from the mere addition, but α-methylthio-α′-chlorostilbene (III). The treatment of 1,2-diphenyl-1-methylthio-2-chloroethane (II) with methanesulfenyl chloride resulted in the formation of III. Thus, II seemed to be an intermediate in the formation of III when I was treated with methanesulfenyl chloride.



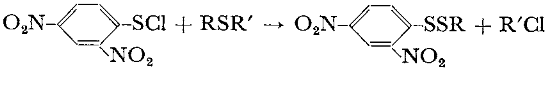
$$C_6H_5CH{=}CHC_6H_5 \xrightarrow{CH_3SCl} C_6H_5\underset{CH_3S}{CH}-\underset{Cl}{CH}C_6H_5$$

(I) (II)

$$\xrightarrow{CH_3SCl} C_6H_5\underset{CH_3S}{C}{=}\underset{Cl}{C}C_6H_5$$

(III)

Since it is rather unusual for methanesulfenyl chloride to dehydrogenate, a series of reactions of sulfenyl chlorides with thioethers has been investigated in order to clarify the nature and the limitations of the reaction. A search of the literature at the outset indicated that, although there were some examples[2] of the reaction of disulfides with sulfenyl chlorides, there was only one paper concerning the reaction between thioethers and sulfenyl chloride;[*1] Moor and Porter[3] reported the formation of alkyl chlorides as the major product when thioethers were treated with 2,4-dinitrobenzenesulfenyl chloride in acetic acid.



The purpose of this paper is to discuss the scope of the reaction, showing the various aspects of the reaction which result from the structural influences.

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[1] M. Ōki and A. Nakamura, unpublished work.

[2] C. G. Moor and M. Porter, *J. Chem. Soc.*, **1958**, 2890.

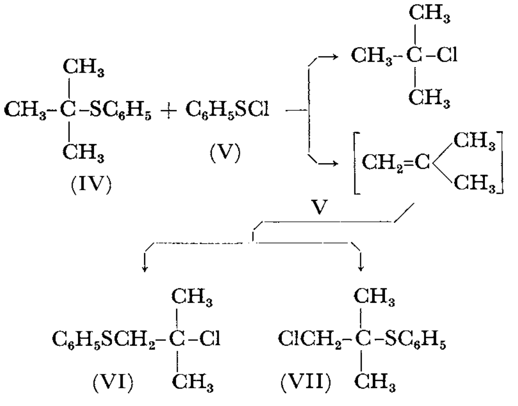
[*1] However, another paper was published concerning the reaction between sulfides and sulfenyl chlorides during the progress of this work. See Ref. 10.

[3] C. G. Moor and M. Porter, *Tetrahedron*, **9**, 58 (1960).

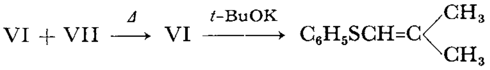
Results and Discussion

Various unsymmetrical thioethers were allowed to react with *ca.* 2 mol benzenesulfenyl chloride (V) in carbon tetrachloride at room temperature. A spontaneous reaction set in, and the evolution of hydrogen chloride was observed. At the completion of the reaction, the red color of the solution of benzenesulfenyl chloride changed to a pale yellow and then did not change any more. The reaction products were analyzed, together with the yields based on the starting thioethers, by intergrating the NMR spectra and gas chromatography of the crude reaction mixture, the behavior of each reaction product being examined beforehand. When possible, the products were isolated by fractional distillation or column chromatography and were subjected to NMR, IR, and elementary analyses.

At the outset, it was expected that *t*-butyl phenyl sulfide (IV) might give the simpler results because of its structure, which would also make analyses by NMR easier. The treatment of *t*-butyl phenyl sulfide with benzenesulfenyl chloride gave 71% *t*-butyl chloride, as was anticipated from an earlier work,[3] and 29% β-chloro sulfides, VI and VII, in approximately 2 : 3 ratio. The formation of VI and VII may be expected if it is assumed that the reaction proceeds *via* the *t*-butyl cation, since the cation will give isobutylene together with the substitution product. The addition of benzenesulfenyl chloride to isobutylene will result in the formation of 2-chloro-2-methyl-1-phenylthiopropane (VI) and of 1-chloro-2-methyl-2-phenylthiopropane (VII).



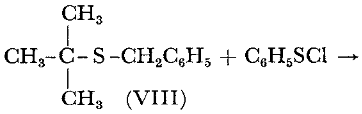
Indeed, the addition of benzenesulfenyl chloride to isobutylene in carbon tetrachloride at room temperature took place exothermally, and the resulting product distribution of VI and VII was in fair agreement with that of the products derived from the reaction of benzenesulfenyl chloride with *t*-butyl phenyl sulfide. The structures of the addition products, which were isomeric mixtures of Markownikoff and anti-Markownikoff adducts, were confirmed by the spectral evidence and by the treatment of the distilled product with potassium *t*-butoxide. On the distillation of the mixture under reduced pressure, isomerization took place and the only isolable compound was 2-chloro-2-methyl-1-phenylthiopropane (VI). Thus, treating the distillate with the base yielded pure 2-methyl-1-phenylthiopropene as a result of dehydrochlorination.



$$\mathrm{VI + VII \xrightarrow{\Delta} VI \xrightarrow{\mathit{t}\text{-BuOK}} C_6H_5SCH{=}C(CH_3)_2}$$

The facts suggest that the adduct VII is formed by the kinetic control and that VII then rearranges to the thermodynamically more stable VI, probably *via* the episulfonium ion intermediate, as has been suggested in an earlier paper,[4] although the reason for the stability of VI is not well understood at present.

The cleavage of the carbon-sulfur bond observed in the reaction of *t*-butyl phenyl sulfide with sulfenyl chloride should be generally observed if the reaction involves the formation of relatively stable carbonium ion. Thus, benzyl *t*-butyl sulfide (VIII) was treated with benzenesulfenyl chloride to give *t*-butyl chloride and the two adducts, VI and VII, in *ca.* 30% and 57% yields respectively. The stoichiometry of the reaction suggests that benzyl phenyl disulfide should be formed, and, indeed, the unsymmetric disulfide was isolated by column chromatography.



(VIII)

$$\mathrm{(CH_3)_3C{-}S{-}CH_2C_6H_5 + C_6H_5SCl \rightarrow}$$

$$\mathrm{C_6H_5CH_2SSC_6H_5}, \textit{etc.}$$

The carbon-sulfur cleavage in benzyl *t*-butyl sulfide occurs predominantly on the *t*-butyl side, giving only 8% benzyl chloride at most. The results conform with the other data on solvolysis,[5] which suggest that the *t*-butyl cation is more easily formed than the benzyl cation. Therefore, it seemed that it would be interesting to ascertain what happens with a sulfide having two alkyl groups which are both poor in giving stable carbonium ions. Benzyl methyl sulfide was, then, treated with benzenesulfenyl chloride. The result was the formation of 9% benzyl chloride and 30% α-chlorobenzyl methyl sulfide. A compound of the latter type is known to be a common product when sulfides are treated with chlorinating agents, such as chlorine,[6] sulfuryl chloride,[7] thionyl

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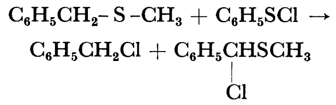
4) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968).

5) C. R. Strauss, H. G. Guay and H. J. Harwood, *J. Org. Chem.*, **29**, 1945 (1964).

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

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

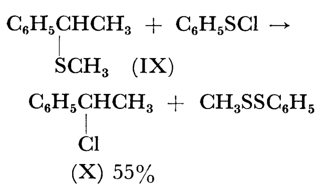
chloride,[8] and *N*-chlorosuccinimide.[9]



$$C_6H_5CH_2\text{-}S\text{-}CH_3 + C_6H_5SCl \rightarrow C_6H_5CH_2Cl + C_6H_5\underset{\displaystyle Cl}{\underset{|}{C}}HSCH_3$$

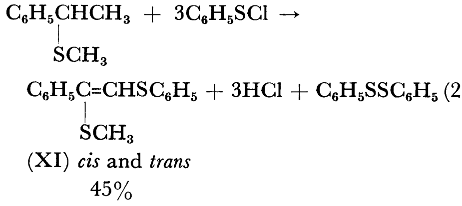
When methanesulfenyl chloride was used in place of V, α-chlorobenzyl methyl sulfide was obtained in a better yield (78%) than in the case of V, and benzyl chloride was also obtained in a 10% yield. Oda and Hayashi have also reported similar results during the course of this study.[10]

The treatment of methyl α-phenethyl sulfide (IX) with V gave 55% α-phenethyl chloride (X). However, neither styrene nor α-chloro-β-phenylthioethylbenzene, which would be expected if styrene were formed and if the addition of V were to follow, was detected in the products. Instead, two unexpected olefins were found by NMR spectra: signals at τ 3.53 and τ 3.83 with relative intensities of *ca.* 3 : 1 and in a 45% yield. Since the elementary analyses of the mixture isolated by alumina chromatography agreed with the $C_{15}H_{14}S_2$ formula, it was assumed that this oily product was an isomeric mixture of the *cis* and *trans* olefinic compounds (XI). The NMR data (τ 3.53, 8.08 and τ 3.83, 8.02 besides the aromatic protons) also agreed with the above.



$$C_6H_5\underset{\displaystyle SCH_3\ (IX)}{\underset{|}{C}}HCH_3 + C_6H_5SCl \rightarrow C_6H_5\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 + CH_3SSC_6H_5 \qquad (1)$$

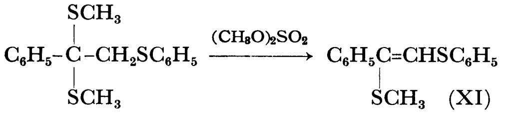
(X) 55%



$$C_6H_5\underset{\displaystyle SCH_3}{\underset{|}{C}}HCH_3 + 3C_6H_5SCl \rightarrow C_6H_5\underset{\displaystyle SCH_3}{\underset{|}{C}}{=}CHSC_6H_5 + 3HCl + C_6H_5SSC_6H_5 \quad (2)$$

(XI) *cis* and *trans*
45%

The structure of XI was unambiguously determined by a comparison of the spectra with an authentic specimen prepared from α-phenylthioacetophenone dimethylmercaptal and dimethyl sulfate according to the published directions:[11]



$$C_6H_5\text{-}\overset{\displaystyle SCH_3}{\underset{\displaystyle SCH_3}{C}}\text{-}CH_2SC_6H_5 \xrightarrow{(CH_3O)_2SO_2} C_6H_5\underset{\displaystyle SCH_3}{\underset{|}{C}}{=}CHSC_6H_5\ (XI)$$

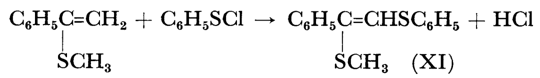
In order to examine the stoichiometry of this unusual olefin-forming reaction, the yields of the products were determined. Typical results from 0.030 mol of methyl α-phenethyl sulfide and 0.079 mol of benzenesulfenyl chloride are presented in Table 1. One point which warrants special attention is the formation of 149% of the hydrogen chloride. Since the formation of α-phenethyl chloride (Eq. (1)) does not need to liberate hydrogen chloride, the formation of 1 mol of the olefin should liberate 3 mol of hydrogen chloride. This treatment of the results also agrees with the distribution of the other products. Thus, Eq. (2) can be written for the formation of the olefin XI.

TABLE 1. PRODUCT DISTRIBUTION OF THE REACTION BETWEEN BENZENESULFENYL CHLORIDE AND METHYL α-PHENETHYL SULFIDE IN CARBON TETRACHLORIDE AT 0°C

Compound	Yield[a] (%)
$C_6H_5CHClCH_3$	55 (b)
$CH_3SSC_6H_5$	55 (b)
HCl	149 (c)
$C_6H_5C(SCH_3){:}CHSC_6H_5$	45 (b)
$C_6H_5SSC_6H_5$	18 (d)

a) Yields based on methyl α-phenethyl sulfide.
b) NMR analysis.
c) Determined by titration.
d) Isolated yield based on benzenesulfenyl chloride. This does not have much significance, since excessive benzenesulfenyl chloride gives diphenyl disulfide during the work up.

Although the formation of the olefin XI may seem very curious, it can be explained by considering the process to involve the addition of the sulfenyl chloride or sulfenyl cation to α-methylthiostyrene, followed by dehydrochlorination or by the removal of a proton. In fact, the treatment of α-methylthiostyrene with equimolar benzenesulfenyl chloride in carbon tetrachloride at room temperature readily afforded a *cis* and *trans* mixture[*2] of the olefin XI, the distribution of which closely agreed with that formed in the reaction of methyl α-phenethyl sulfide. Hydrogen chloride was evolved during the course of the reaction. The above assumption can, then, be fairly well verified if the formation of α-methylthiostyrene during the reaction can be proved.



$$C_6H_5\underset{\displaystyle SCH_3}{\underset{|}{C}}{=}CH_2 + C_6H_5SCl \rightarrow C_6H_5\underset{\displaystyle SCH_3}{\underset{|}{C}}{=}CHSC_6H_5 + HCl\ (XI)$$

The above discussion leads to the idea that some sulfides are dehydrogenated to form vinyl sulfide derivatives. This is in conformity with the observation in the reaction of stilbene and an excess of methanesulfenyl chloride[1] and suggests that the

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[8] W. E. Truce, G. Birum and E. T. McBee, *ibid.*, **74**, 3594 (1952).

[9] D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969).

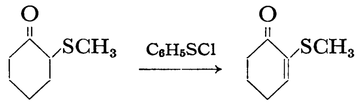
[10] R. Oda and Y. Hayashi, *Tetrahedron Lett.*, **1967**, 3141.

[11] J. Gosselck, L. Beress, H. Schenk and G. Schmidt, *Angew. Chem.*, **77**, 1140 (1965).

[*2] As for the assignment of the configuration, see This Bulletin, **43**, 1234 (1970).

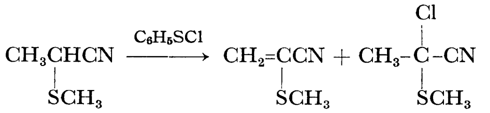
dehydrogenation of thioethers by sulfenyl chlorides is a fairly general reaction. However, in order to isolate the olefin intermediate, the olefin must be fairly inert toward the addition reaction of sulfenyl chloride. Thus, some other sulfides were treated with benzenesulfenyl chloride in an attempt to isolate the intermediate.

The olefinic linkage in an α,β-unsaturated carbonyl compound will be less reactive than the ordinary olefins toward the electrophilic attack because of the lower electron density. Thus, some α-methylthio ketone would give the α-methylthio-α,β-unsaturated ketone in the reaction with sulfenyl chloride. α-Methylthiocyclohexanone (XII) was treated with benzenesulfenyl chloride; as expected, 2-methylthio-2-cyclohexen-1-one (XIII) was isolated in a 40% yield. The structue of XIII was established on the basis of the spectral evidence and by the characterization of its 2,4-dinitrophenylhydrazone.

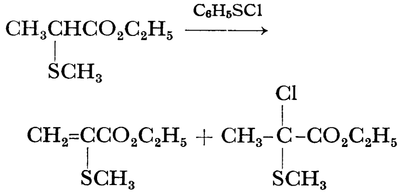


(XII) (XIII)

Other electron-deficient olefins, such as α-methylthioacrylonitrile and ethyl α-methylthioacrylate, were also detected when the corresponding nitrile and ester were treated with the sulfenyl chloride, although, in these cases, substitution by chlorine at the α-position was the main reaction.

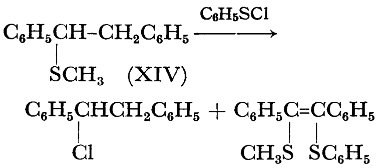


$$\underset{SCH_3}{CH_3CHCN} \xrightarrow{C_6H_5SCl} \underset{SCH_3}{CH_2{=}CCN} + CH_3\text{-}\overset{Cl}{\underset{SCH_3}{C}}\text{-}CN$$



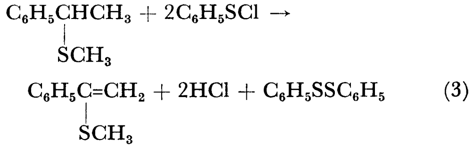
$$\underset{SCH_3}{CH_3CHCO_2C_2H_5} \xrightarrow{C_6H_5SCl}$$
$$\underset{SCH_3}{CH_2{=}CCO_2C_2H_5} + CH_3\text{-}\overset{Cl}{\underset{SCH_3}{C}}\text{-}CO_2C_2H_5$$

If 1,2-diphenylethyl methyl sulfide (XIV) is analogously dehydrogenated, it will give α-methylthiostilbene. However, XIV gave 30% corresponding chloride (XV) and 65% *cis*- and *trans*-α-methylthio-α'-phenylthiostilbene (XVI), the latter being formed by the addition of benzenesulfenyl chloride to α-methylthiostilbene, followed by dehydrochlorination (or by the addition of the sulfenyl cation, followed by the removal of the proton). These results indicate that the intermediate α-methylthiostilbene is too reactive to be isolated.



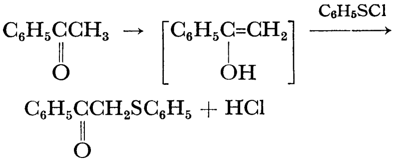
$$\underset{SCH_3\ (XIV)}{C_6H_5CH\text{-}CH_2C_6H_5} \xrightarrow{C_6H_5SCl}$$
$$\underset{(XV)}{\underset{Cl}{C_6H_5CHCH_2C_6H_5}} + \underset{(XVI)}{\underset{CH_3S\ \ SC_6H_5}{C_6H_5C{=}CC_6H_5}}$$

From these data it is now apparent that the vinyl sulfide derivative intervenes in these reactions and that the following equation, Eq. (3), can be written as a part of the reaction represented by Eq. (2):

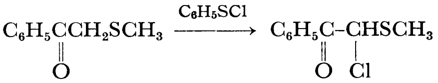


$$\underset{SCH_3}{C_6H_5CHCH_3} + 2C_6H_5SCl \rightarrow$$
$$\underset{SCH_3}{C_6H_5C{=}CH_2} + 2HCl + C_6H_5SSC_6H_5 \qquad (3)$$

As to the oxidative chlorination of thioethers by sulfenyl chloride, there is another interesting example of the reaction. That is, α-methylthioacetophenone, which is not capable of undergoing dehydrogenation because of its structure, gives an almost quantitative yield of α-chloro-α-methylthioacetophenone. This is very interesting in that, while acetophenone gives α-phenylthioacetophenone when treated with benzenesulfenyl chloride, α-methylthioacetophenone does not give α-phenylthio-α-methylthioacetophenone. If only the enolization and addition are taken into account, α-methylthioacetophenone should have given α-phenylthio-α-methylthioacetophenone more easily. It seems that the sulfur atom in thioether is more vulnerable to attack in this case.



$$\underset{O}{\underset{\|}{C_6H_5CCH_3}} \rightarrow \left[\underset{OH}{\underset{|}{C_6H_5C{=}CH_2}}\right] \xrightarrow{C_6H_5SCl}$$
$$\underset{O}{\underset{\|}{C_6H_5CCH_2SC_6H_5}} + HCl$$



$$\underset{O}{\underset{\|}{C_6H_5CCH_2SCH_3}} \xrightarrow{C_6H_5SCl} \underset{O\ \ Cl}{C_6H_5C\text{-}CHSCH_3}$$

This oxidative chlorination may be classified as a Pummerer-type reaction,[12] which now seems to be a general term for a whole class of reactions involving the reduction of a sulfonium salt with the concomitant oxidation of the α-carbon.

It is thus established that three general types of reactions can occur for thioethers when they are treated with sulfenyl chlorides.

The first is an S_N1-type reaction on the sp^3 carbon atom where the cleavage of the carbon-sulfur bond takes place to produce the carbonium ion, followed by a nucleophilic attack by the chloride ion or by the removal of one of the α-hydrogens as a proton. This type of reaction was observed in the thioethers which carry alkyl groups which tend to give stable carbonium ions, such as the *t*-butyl cation. However, there is definitely another S_N2-type displacement of the alkylthio group by chlorine, for the treatment of optically active 1-phenyl-1-methylthiopropane with methanesulfenyl chloride gave

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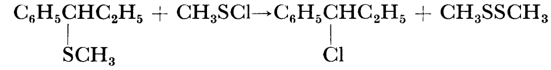
[12] G. A. Russell and G. J. Mikol, "Mechanisms of Molecular Migrations," Vol. 1, Interscience Publishers, New York (1968), p. 157.

1-phenyl-1-chloropropane with an inverted configuration (see the Experimental part). The failure to detect styrene or its adduct in the reaction of methyl α-phenethyl sulfide could lend support to this proposition. This reaction seems to occur when the alkyl part gives a less stable carbonium ion.



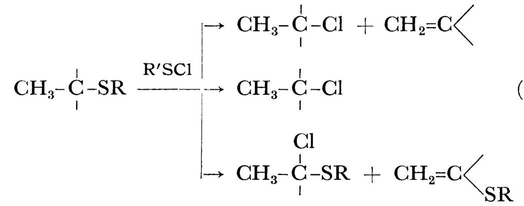
$$\underset{SCH_3}{C_6H_5CHC_2H_5} + CH_3SCl \rightarrow \underset{Cl}{C_6H_5CHC_2H_5} + CH_3SSCH_3$$

inversion of configuration

The second type of reaction is the displacement of the α-hydrogen of the thioethers by chlorine to give α-chloro sulfide *i. e.*, oxidative chlorination. This reaction seems to take place when the carbonium ion alpha to sulfur is rather unstable and picks up the chloride anion before losing the proton. If the carbonium ion cannot lose the proton due to its inherent structure, this reaction takes place almost quantitatively.

The third type of reaction is the dehydrogenation which takes place competitively with the second type. It seems that dehydrogenation takes place preferentially when the carbonium ion alpha to sulfur is rather stable or when the product is stabilized by conjugation.

These three reactions may be summarized as in Eq. (4):



(4)

It is not well understood what type of atom is necessary to induce these types of reactions with sulfenyl chlorides. However, the data accumulated in this laboratory indicate that chlorine and oxygen do not induce these reactions. That is, stilbene dichloride, α-phenethyl chloride, and benzyl ethyl ether failed to react with either benzene- or methanesulfenyl chloride.

Experimental

Starting Materials. Benzenesulfenyl chloride was prepared according to the published directions[13] and was always distilled prior to use. The thioethers, other than those indicated below, were prepared by methods that have already been described, and their physical constants were checked.

α-Methylthiostyrene. 1,2-Bis(methylthio)ethylbenzene[14] (45 g) was added to a solution of potassium *t*-butoxide prepared from 10 g of potassium and 400 m*l* of *t*-butyl alcohol, after which the mixture was heated under reflux for 3 hr. After the *t*-butyl alcohol had mostly been removed by distillation from the mixture, the remaining liquid was poured into 300 m*l* of water and extracted with ether. The ethereal extract was dried over anhydrous sodium sulfate and distilled to give 25 g of α-methylthiostyrene; bp 69—70°C/2 mmHg, n_D^{25} 1.5905 (lit,[14] n_D^{25} 1.5910). NMR (τ); 7.83 (3H, s), 5.16 (1H, s), 4.68 (1H, s), 2.5—2.9 (5H, m). IR (cm^{-1}); 1226, 1068, 1025, 848, 770, 699.

1,2-Diphenylethyl Methyl Sulfide. Methyl mercaptan (0.2 mol) was introduced at 0°C into a solution prepared from 4.6 g of sodium and 200 m*l* of ethanol. To this solution there was then added, drop by drop, 40 g of 1,2-diphenylethyl chloride in 100 m*l* of ethanol, after which the mixture was stirred under reflux for 10 min. The major portion of the solvent was removed under reduced pressure, and the residual mixture was extracted with ether after pouring it into 300 m*l* of water. The extract was dried over anhydrous sodium sulfate and distilled to afford 34 g of 1,2-diphenylethyl methyl sulfide; bp 151—152°C/3 mmHg, n_D^{28} 1.5938. NMR (τ); 8.29 (3H, s), 6.22 (1H) and 6.95 (2H) A_2X pattern, $J_{AX}=8$ Hz, 2.88 (5H, s), 3.0 (5H, m). IR (cm^{-1}); 1073, 1032, 768, 750, 730, 700, 543, 530. Found: C, 78.94; H, 7.06%. Calcd for $C_{15}H_{16}S$: C, 78.89; H, 7.07%.

General Procedure for the Reaction and the Product Analyses. To an approximately 0.2M solution of the thioether in carbon tetrachloride, *ca.* 2 mol benzenesulfenyl chloride was added at room temperature under anhydrous conditions. After the reaction had been completed, the reaction mixture was poured into an aqueous solution of sodium bicarbonate and extracted with additional carbon tetrachloride. After the removal of most of the solvent under reduced pressure, the crude products were analyzed by NMR spectroscopy, and then any unknown products were isolated by distillation or by column chromatography. The reaction mixture before the removal of the solvent was examined by gas chromatography as required. An essentially quantitative consumption of the thioether was observed. Each product other than the known products was identified as will be described below.

Adducts of Benzenesulfenyl Chloride to Isobutylene. Isobutylene was slowly introduced into a carbon tetrachloride solution of benzenesulfenyl chloride at −10—0°C. The complete fading of the orange color indicated the completion of the reaction. After the solvent had then been removed under reduced pressure, the crude reaction mixture showed NMR signals for two isomers with a relative intensity of *ca.* 3 : 2; this was in fair agreement with that of the products from *t*-butyl phenyl sulfide and benzenesulfenyl chloride. In order to obtain analytical samples of the isomeric mixture, the adducts were distilled *in vacuo* when the distillate contained only one isomer. This isomer was found to be the Markownikoff adduct from the following data and from the dehydrochlorination to be described below. Bp 97°C/3 mmHg, n_D^{25} 1.5597 (lit,[15] bp 59—60°/3 mmHg, n_D^{23} 1.5661). NMR (τ); 8.45 (6H, s), 6.78 (2H, s), 2.7—3.1 (5H, m). IR (cm^{-1}); 1579, 1107, 1090, 740, 693, 615, 568. Found: C, 60.03; H, 6.24%. Calcd for

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$C_{10}H_{13}ClS$: C, 59.84; H, 6.53%.

The other product which disappeared on distillation had NMR signals at τ 8.62 (6H, s) and 6.48 (2H, s), the lower chemical shift of CH_2 supporting the assigned structure.

The distillate (9 g) was heated under reflux for 30 min with a solution prepared from 2 g potassium and 80 m*l* of *t*-butyl alcohol. After the usual work-up, the distillation of the product gave 5.1 g of 2-methyl-1-phenylthiopropene; bp 88°C/4 mmHg, n_D^{20} 1.5791 (lit,[16] n_D^{25} 1.5782). NMR (τ): 8.22 (3H, s), 8.20 (3H, d), 4.32 (1H, m), 3.05 (5H, m). IR (cm^{-1}): 1580, 803, 738, 690.

Benzyl Phenyl Disulfide. The crude mixture obtained from the reaction of benzyl *t*-butyl sulfide and benzenesulfenyl chloride was chromatographed on alumina to give the pure disulfide; $n_D^{28.5}$ 1.6409. NMR (τ): 6.32 (2H, s), 2.8—3.2 (10H, m). IR (cm^{-1}): 1070, 1027, 689, 567. Found: C, 67.19; H, 5.04%. Calcd for $C_{13}H_{12}S_2$: C, 67.17; H, 5.21%.

Methyl Phenyl Disulfide. The product from methyl α-phenethyl sulfide and benzenesulfenyl chloride was chromatographed on alumina. The disulfide was eluted as a yellow oil with petroleum ether; $n_D^{26.5}$ 1.6125. NMR (τ): 7.72 (3H, s), 2.7—3.2 (5H, m). IR (cm^{-1}): 1027, 955, 742, 693. Found: C, 53.75; H, 5.31%. Calcd for $C_7H_8S_2$: C, 53.80; H, 5.16%.

***cis*-and *trans*-α-Methylthio-β-phenylthiostyrenes.** This olefin was eluted with petroleum ether in a later fraction on the alumina chromatography of the product from the above-mentioned reaction. NMR (τ): 8.08 (3H, s), 3.53 (1H, s), 2.6—3.3 (10H, m) and 8.02 (3H, s), 3.83 (1H, s), 2.6—3.3 (10H, m). IR (cm^{-1}): 806, 758, 740, 698, 690. Found: C, 69.36; H, 5.33%. Calcd for $C_{15}H_{14}S_2$: C, 69.70; H, 5.46%.

***cis*-and *trans*-α-Methylthio-α′-phenylthiostilbenes.** An isomeric mixture of the olefin was isolated by alumina chromatography from the reaction mixture obtained from 1,2-diphenylethyl methyl sulfide and benzenesulfenyl chloride. NMR (τ): 8.17 (3H, s), 2.5—3.3 (15H, m) and 8.31 (3H, s), 2.5—3.3 (15H, m). IR (cm^{-1}): 1075, 1027, 738, 699, 582. Found: C, 75.41; H, 5.50%. Calcd for $C_{21}H_{18}S_2$: C, 75.41; H, 5.42%.

α-Chlorobenzyl Methyl Sulfide. Although this sulfide was not isolated, the NMR spectrum of the reaction mixture from benzyl methyl sulfide and benzenesulfenyl chloride showed the existence of the sulfide by the signals at τ 7.75 (3H, s) and 4.03 (1H, s); these signals were situated at the same positions as those of the chlorinated products of benzyl methyl sulfide with chlorine[6] or methanesulfenyl chloride.[10] When methanesulfenyl chloride was used, the reaction products were directly treated with 2,4-dinitrophenylhydrazine in acetic acid; the product was identified with the 2,4-dinitrophenylhydrazone of benzaldehyde (mp 237°C).

2-Methylthio-2-cyclohexen-1-one. The product from the reaction of α-methylthiocyclohexanone and benzenesulfenyl chloride was eluted with benzene through an alumina column to give crude 2-methylthio-2-cyclohexen-1-one, which showed an olefinic proton signal at τ 3.49 (triplet, *J*=4.5 Hz) in NMR and an absorption at 1679 cm^{-1} in IR.

When the crude product was treated with 2,4-dinitrophenylhydrazine, pure 2,4-dinitrophenylhydrazone of 2-methylthio-2-cyclohexen-1-one was obtained as dark red crystals; mp 222—224°C. NMR (τ): 7.66 (3H, s), 7.2—8.1 (6H, m), 3.78 (1H, t, *J*=4.5 Hz), aromatic protons (3H, m). IR (cm^{-1}): 3310, 848, 745. Found: C, 48.69; H, 4.65; N, 17.63%. Calcd for $C_{13}H_{14}O_4N_4S$: C, 48.44; H, 4.38; N, 17.38%.

α-Chloro-α-methylthiopropionitrile and α-Methylthioacrylonitrile. The NMR spectrum of the product from the reaction of α-methylthiopropionitrile showed two 1 : 1 singlets at τ 7.78 and 7.47 as the major component (90% yield). The formation of an olefinic compound in a small quantity (*ca.* 5%) was observed from the NMR signals at τ 3.99 (1H, d), 4.23 (1H, d), and 7.68 (3H, s); this compound was identified as α-methylthioacrylonitrile by comparing its NMR with that of an authentic sample prepared as described in the literature.[17] The major product was distilled under reduced pressure (29°C/4 mmHg); it was identified as α-chloro-α-methylthiopropionitrile from the spectroscopic data. IR (cm^{-1}): 2250, 720, 690. Treating this compound with 2,4-dinitrophenylhydrazine in ethanol and a small amount of sulfuric acid gave red crystalline hydrazone of pyruvonitrile; mp 185—186°C. NMR (τ): 7.61 (3H, s), aromatic proton (3H, m). IR (cm^{-1}): 3305, 2235, 850, 840, 745, 723, 600. Found: C, 43.41; H, 2.59; N, 28.35%. Calcd for $C_9H_7N_5O_4$: C, 43.38; H, 2.83; N, 28.10%.

Ethyl α-Chloro-α-methylthiopropionate and Ethyl α-Methylthioacrylate. The major component (40%) of the products was found to be ethyl α-chloro-α-methylthiopropionate by a study of the NMR spectrum of the crude reaction mixture (τ 8.02, τ 7.76, and ethyl protons). The ester was easily hydrolyzed to give ethyl pyruvate. The distillate (bp 28—43°C/5 mmHg), which contained the above product as the major component, was directly treated with 2,4-dinitrophenylhydrazine; the 2,4-dinitrophenylhydrazone of ethyl pyruvate was thus obtained; mp 155°C (lit,[18] mp 153°C). The structure of the olefinic product, which was obtained in a 15% yield, was assigned on the basis of a study of the NMR spectrum and from analogy with a previous example:[19] when the addition products of methanesulfenyl chloride to ethyl acrylate were dehydrochlorinated with an excess of triethylamine in carbon tetrachloride at 0°C, only the anti-Markownikoff adduct gave off hydrogen chloride to form ethyl α-methylthioacrylate, and the Markownikoff adduct was left intact. The NMR spectrum of the resulting products showed the signal of an olefinic compound at the same position as that of the product from the reaction of ethyl α-methylthiopropionate: τ 4.85 (s) and τ 3.75 (s).

α-Chloro-α-methylthioacetophenone. The NMR signals (τ 7.94, τ 3.65, and phenyl protons) of the product obtained from the reaction between α-methylthioacetophenone and benzenesulfenyl chloride agreed with those of the reaction product from α-methylsulfinylacetophenone and thionyl chloride,[20] and also with those

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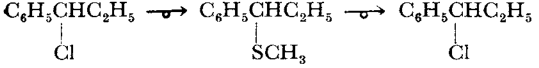
of the product of the reaction between α-methylthioacetophenone and methanesulfenyl chloride.[21] The latter reaction was reported to give α-chloro-α-methylthioacetophenone.

Stereochemical Study of the Substitution Reaction. Optically active methyl 1-phenylpropyl sulfide was prepared from (−)-1-phenylpropyl chloride and methyl mercaptide. The stereochemical outcome must be inversion in this reaction. The treatment of the resulting (+)-sulfide with methanesulfenyl chloride afforded (−)-1-phenylpropyl chloride. Thus, the inversion of configuration must have taken place in this reaction, although racemization was observed to some extent.



$$\underset{\text{Cl}}{C_6H_5\underset{|}{C}HC_2H_5} \xrightarrow{CH_3S^{\ominus}} \underset{\text{SCH}_3}{C_6H_5\underset{|}{C}HC_2H_5} \xrightarrow{CH_3SCl} \underset{\text{Cl}}{C_6H_5\underset{|}{C}HC_2H_5}$$

(−)-1-Phenylpropyl Chloride. The racemic 1-phenylpropyl alcohol was resolved by the fractional crystallization of the strychnine salt of its hydrogen phthalate, $[\alpha]^{25}_{578}$ −25.53 (neat) (lit,[22] $[\alpha]^{25}_{578}$ −23.413 (neat)), and was treated with thionyl chloride as in the literature.[23] $[\alpha]^{25}_{365}$ −69.84, $[\alpha]^{25}_{436}$ −41.47 (ethanol) (lit,[23] $[\alpha]^{25}_{D}$ −28.9 (neat)).

(+)-Methyl 1-Phenylpropyl Sulfide. An ethanolic solution from 11.5 g of (−)-1-phenylpropyl chloride was treated with sodium methyl mercaptide from 0.075 mol of sodium in 130 m*l* of ethanol at 45°C for 20 min. The reaction mixture was then poured into an aqueous solution (200 m*l*) of sodium chloride and extracted with ether. The distillation of the extract after drying gave 9.3 g of (+)-methyl 1-phenylpropyl sulfide, bp 82°C/5 mmHg, $[\alpha]^{25}_{365}$ +108.49, $[\alpha]^{25}_{436}$ +64.70 (ethanol).

(−)-1-Phenylpropyl Chloride from (+)-Methyl 1-Phenylpropyl Sulfide and Methanesulfenyl Chloride. Methanesulfenyl chloride (3.8 g) was added to a solution of 7.5 g of (+)-methyl 1-phenylpropyl sulfide in 150 m*l* of carbon tetrachloride. After standing for 1 hr at 0°C, the mixture was decomposed with ice water. The organic part was then extracted with ether, dried over sodium sulfate, and distilled under reduced pressure to give 5.2 g of (−)-1-phenylpropyl chloride; $[\alpha]^{25}_{365}$ −47.97, $[\alpha]^{25}_{436}$ −27.61 (ethanol).

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