[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Formation of α-Chloro Sulfides from Sulfides and from Sulfoxides

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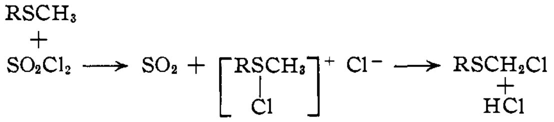
A number of α-chloromethyl sulfides have been prepared by the reaction of sulfides with sulfuryl chloride. The method failed with cyclic sulfides and with most other sulfides containing β-hydrogen. The reaction of sulfoxides with acid chlorides, including thionyl chloride, *p*-nitrobenzoyl chloride and benzoyl chloride, also gave α-chlorosulfides. It is suggested that acid chlorides react with sulfoxides to form acyloxysulfonium chlorides, $[ArS(CH_3)OCOR]^+Cl^-$, which by exchange give chlorosulfonium acid salts, $[ArS(CH_3)Cl]^{+-}OCOR$. Abstraction of a proton from the methyl group by $RCOO^-$ gives the same intermediate, $[Ar\overset{+}{S}(\overset{-}{C}H_2)Cl]$, as is believed to be formed in the chlorination of sulfides with chlorine or sulfuryl chloride. Some experimental evidence supporting this reaction course is presented. An exchange of oxygen between a sulfoxide and a sulfide has been observed.

Chlorination of Sulfides.—As part of a general program of investigation of the methods available for the synthesis of divalent sulfur compounds, we have explored the feasibility of introducing α-alkyl and α-aryl substituents into sulfides by chlorination of the parent sulfide followed by coupling of the resulting α-chlorosulfide with Grignard reagents. It was hoped that this route might be particularly useful for α-substituted cyclic sulfides, since the starting materials for the synthesis of these by ring closure methods are not always easily accessible.

$$RCH_2SCH_2R \xrightarrow{Cl_2} RCHClSCH_2R \xrightarrow{R'MgX} RR'CHSCH_2R$$

The chlorination of sulfides has been described several times in the literature,[2] but usually polychlorinated products were obtained. Lawson and Dawson[3] effected the monochlorination of mustard gas by decomposing the crystalline chlorine–sulfide addition compound (chlorosulfonium chloride), which was isolated at a temperature below 0°. Recently Böhme, Fischer and Frank[4] have obtained four other α-chlorosulfides using this method.

In the present investigation sulfuryl chloride[5] was used to facilitate regulation of the amount of chlorinating agent. The reactions were carried out by addition of sulfuryl chloride in pentane (or methylene chloride) solution to a heated pentane (or methylene chloride) solution containing slightly less than an equimolar quantity of the sulfide. Sulfur dioxide was evolved and a transitory intermediate appeared during the addition. The intermediate, presumably the chlorosulfonium chloride I, was isolated in a few reactions carried out below 0°, and was allowed to decompose at room temperature.



$$\begin{matrix} RSCH_3 \\ + \\ SO_2Cl_2 \end{matrix} \longrightarrow SO_2 + \underset{\text{I}}{\left[\begin{matrix} RSCH_3 \\ | \\ Cl \end{matrix}\right]^+} Cl^- \longrightarrow \begin{matrix} RSCH_2Cl \\ + \\ HCl \end{matrix}$$

The sulfides successfully chlorinated were methyl phenyl, methyl *p*-tolyl, methyl *p*-chlorophenyl, methyl *p*-methoxyphenyl, methyl benzyl, phenyl benzyl, dimethyl, diethyl, methyl *t*-butyl and bis-(carbethoxymethyl). Most of the α-chlorosulfides obtained in this work have been prepared previously by the reaction of hydrogen chloride on a mixture of mercaptan and aldehyde.[4,6] The present method is considerably shorter and the yields are at least as good.

The product from the chlorination of benzyl sulfide decomposed in an attempted distillation at 0.1 mm., but the formation of α-chlorobenzyl benzyl sulfone in an oxidation of a sample of the crude reaction product[7] shows the presence of α-chlorobenzyl benzyl sulfide.

Attempts to obtain discrete products from the chlorination of allyl sulfide, phenyl ethyl sulfide, diisopropyl sulfide, methyl isopropyl sulfide, thiacyclopentane (tetramethylene sulfide), α-methylthiacyclopentane or thiacyclohexane were unsuccessful.

It is significant that, in general, sulfides containing a β-hydrogen fail to yield α-chlorosulfides smoothly. The successful monochlorination of diethyl sulfide is an exception, but, as has been observed previously,[4] the α-chloroethyl ethyl sulfide formed is much less stable than chloromethyl sulfides, turning dark soon after distillation. It seems likely that under the conditions used, α-chlorosulfides containing β-hydrogen were converted to α,β-unsaturated sulfides, which reacted further with the chlorinating agent or polymerized. In line with this, one attempt to chlorinate thiacyclopentane gave a product tentatively identified as 2,3-dichlorothiacyclopentane, and distillation of a chlorination product of thiacyclohexane gave a product believed to be 2-thiacyclohexene.

The facile elimination of hydrogen chloride from α-chlorosulfides is demonstrated by the decomposition of α,β-dichloroethyl β′-chloroethyl sulfide on attempted distillation under vacuum,[3] to give a product later shown[8] to be a mixture of *cis*- and *trans*-β-chlorovinyl β-chloroethyl sulfides. The formation of α,β-dichloro ethers in the chlorination

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[1] American Petroleum Institute Post-doctorate Fellow, 1949–1951. This investigation was conducted as part of API Research Project 48B.

[2] (a) M. A. Riche, *Ann. chim. phys.*, [3] **43**, 283 (1855); (b) T. Zincke and W. Frohenberg, *Ber.*, **42**, 2721 (1909); (c) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 594 (1922).

[3] W. E. Lawson and T. P. Dawson, THIS JOURNAL, **49**, 3119 (1927).

[4] H. Böhme, H. Fischer and R. Frank, *Ann.*, **563**, 54 (1949); see also H. Böhme and H. Gran, *ibid.*, **577**, 68 (1952).

[5] W. E. Truce, G. H. Birum and E. T. McBee, THIS JOURNAL, **74**, 3594 (1952), published their report on the chlorination of dimethyl sulfide with thionyl and sulfuryl chlorides after this investigation had been completed.

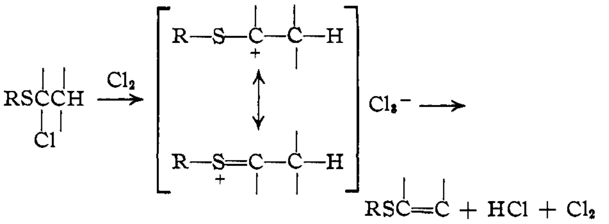
[6] (a) H. Böhme, *Ber.*, **69**, 1610 (1936); (b) L. A. Walter, L. H. Goodson and R. J. Fosbinder, THIS JOURNAL, **67**, 655, 657 (1945).

[7] F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5187 (1951).

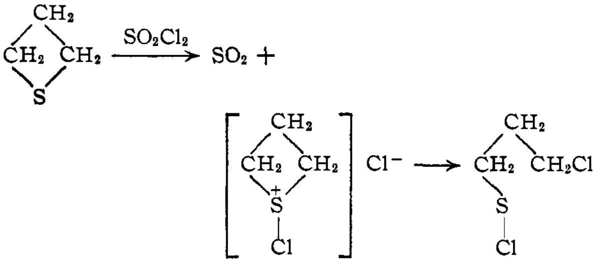
[8] R. C. G. Moggridge, *J. Chem. Soc.*, 1105 (1946).

of ethers also appears to be best accounted for by assuming dehydrochlorination of α-chloro ethers followed by addition of chlorine.[9] The reaction of α-chloro ethers with bromine to give α,β-dibromo ethers,[10] which is an important step in the Boord synthesis of olefins, is another example of dehydrohalogenation followed by halogen addition.

It seems reasonable to suppose that dehydrohalogenations of α-chloro ethers and sulfides are catalyzed by the presence of acid reagents, such as hydrogen halides and halogens. One possible formulation is shown



The presence of colored impurities in several of the distillates suggested contamination by sulfenyl chlorides, especially since the colors were discharged by the addition of acetone. Attempts to prepare 1,1-dimethylethanesulfenyl chloride [$(CH_3)_3CSCl$] by the chlorination of *t*-butyl sulfide or *t*-butyl phenyl sulfide were unsuccessful, however. With thiacyclobutane and sulfuryl chloride chlorinolysis did occur and γ-chloropropanesulfenyl chloride (II) was the major product[11]; II probably was formed by the nucleophilic attack of chloride



II

ion on carbon in the chlorosulfonium ion shown.[12] The ring opening suggests strain in the four-membered ring.

The coupling of α-chloro sulfides with Grignard reagents, which has been reported previously only in one instance,[6a] was found to proceed in good yield. The structures of the α-chloro sulfides usually were established through this reaction by comparison of the properties of derivatives of the α-phenyl sulfides obtained from coupling with phenylmagnesium bromide with those of known compounds. With phenyl chloromethyl sulfide and *t*-butylmagnesium chloride no coupling product was isolated, the "reduction" product, phenyl methyl sulfide, together with isobutylene being produced in part.[13] Similarly the coupling between phenyl chloromethyl sulfide and the secondary Grignard reagents, isopropylmagnesium bromide or cyclohexylmagnesium bromide, was not smooth. However, the coupling of cyclohexylmagnesium bromide with α-chlorobenzyl methyl sulfide was observed to proceed in good yield.

Chloromethyl phenyl and chloromethyl *p*-tolyl sulfides reacted spontaneously with magnesium in ether solution to give the coupling products, 1,2-bis-(phenylmercapto)-methane and 1,2-bis-(*p*-tolylmercapto)-methane. Surprisingly, this reaction could not be initiated using chloromethyl methyl sulfide, chloromethyl *t*-butyl sulfide or α-chlorobenzyl methyl sulfide.

Chlorination of Sulfoxides.—The formation of α-chloro sulfides was accomplished also by the reaction of sulfoxides with thionyl chloride

$$RSOCH_3 + SOCl_2 \longrightarrow RSCH_2Cl + SO_2 + HCl$$

With dimethyl, methyl phenyl, methyl *p*-chlorophenyl, methyl benzyl, diethyl and methyl *t*-butyl sulfoxides the yield of α-chlorosulfides was at least as high as that obtained from the corresponding sulfides and sulfuryl chloride. The reaction failed to give discrete products when applied to thiacyclopentane or thiacyclohexane 1-oxides, and with benzyl sulfoxide the only product identified was a small amount of benzaldehyde. Phenyl vinyl sulfide was obtained in 31% yield from ethyl phenyl sulfoxide and thionyl chloride; washing the chlorination product with dilute alkali prior to distillation increased the yield to 60%. The isolation of phenyl vinyl sulfide in these reactions once again testifies to the instability and reactivity of α-chlorosulfides containing a β-hydrogen.

The reaction of methyl phenyl sulfoxide with *p*-nitrobenzoyl chloride in benzene solution also gave chloromethyl phenyl sulfide

$$C_6H_5SOCH_3 + p\text{-}NO_2C_6H_4COCl \longrightarrow C_6H_5SCH_2Cl + p\text{-}NO_2C_6H_4COOH$$

A similar type of reaction was indicated for methyl benzyl sulfoxide, thiacyclopentane 1-oxide and ethyl phenyl sulfoxide under comparable conditions by the nearly quantitative precipitation of *p*-nitrobenzoic acid. Phenyl vinyl sulfide was isolated from the reaction involving phenyl ethyl sulfoxide. Methyl sulfoxide and benzoyl chloride gave chloromethyl methyl sulfide.

Discussion

The formation of chlorosulfonium chlorides in the chlorination of sulfides frequently has been observed. It seems most reasonable to assume that chlorination of the sulfide is effected by abstraction of a proton by the chloride ion from the chlorosulfonium ion to give an intermediate III, which can readily rearrange to an α-chlorosulfide IV.

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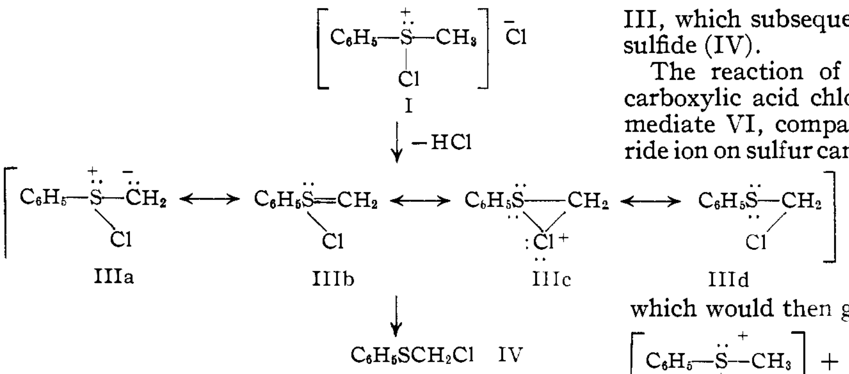
[9] R. K. Summerbell and L. N. Bauer, This Journal, **57**, 2364 (1935); G. E. Hall and F. M. Ubertine, *J. Org. Chem.*, **15**, 715 (1950).

[10] L. C. Swallen and C. E. Boord, This Journal, **52**, 651 (1930).

[11] A similar result was recently observed by J. M. Stewart and C. H. Burnside, *ibid.*, **75**, 243 (1953).

[12] Several other instances of chlorinolysis of sulfides have been observed. Examples are the formation of 30–45% of α-phenethyl chloride in the reaction of sulfuryl chloride with α-phenethylmercaptoacetic acid (B. Holmberg, *Arkiv Kemi Mineral. Geol.*, **14A**, No. 2 (1940)), the obtention of 2-nitro-4-methylbenzenesulfenyl chloride from the reaction of methyl 2-nitro-4-methylphenyl sulfide and chlorine (T. Zincke and H. Röse, *Ann.*, **406**, 127 (1914)), and the formation of perchloromethylmercaptan, Cl_3CSCl, and *t*-butyl chloride in the reaction of sulfuryl chloride with *t*-butyl trichloromethyl sulfide (see ref. 5).

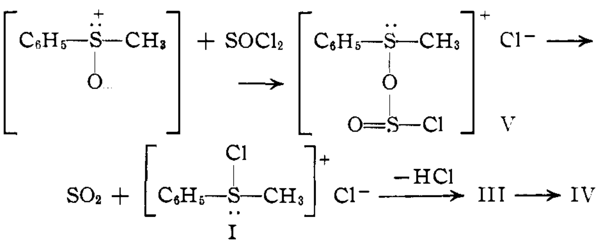
[13] M. Knell, Ph.D. Dissertation, Northwestern University, 1949, reported that in the reaction of chloromethyl benzyl sulfide with *t*-butylmagnesium chloride methyl benzyl sulfide was the major product (50%).



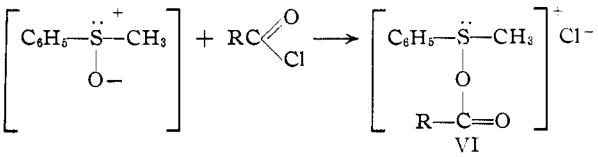
One might say that, in going from I to $C_6H_5SCH_2Cl$ *via* III, a chloronium ion "rides downhill from sulfur to carbon on an electron cloud."[14] The relationship between structure IIId and IV is rather unusual. Structure IIId, which is a representation of one of the resonance forms of III, is a high energy form of IV in which the chlorine has a fixed position relative to the carbon and sulfur atoms.

It is of interest to note that chlorination occurs exclusively in the $-S-CH_3$ side chain even in *p*-methoxyphenyl methyl sulfide, where the aromatic nucleus is strongly activated.

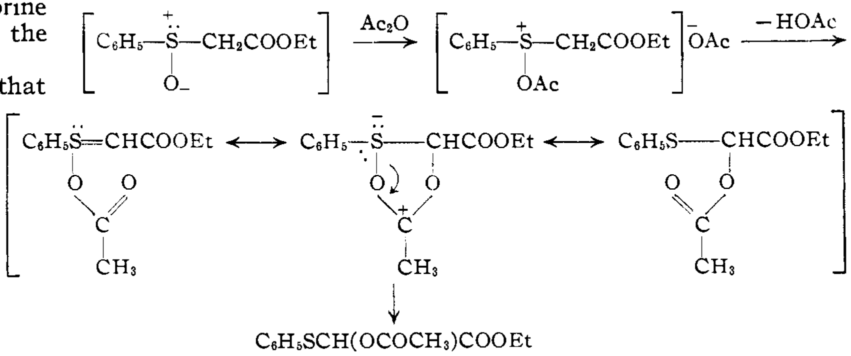
Sulfoxides are basic as is indicated by their ability to form salts with strong acids,[15] their hygroscopic nature and their ability to form strong hydrogen bonds. The salts formed with strong acids may be regarded as sulfonium salts, and the reactions observed by us are perhaps best interpreted as involving sulfonium salt intermediates. Thus, the reaction of phenyl methyl sulfoxide with thionyl chloride may involve the formation of sulfonium salt V. The ^-OSOCl group may be displaced (giving SO_2 and Cl^-) by attack of chloride ion on sulfur, the product being I. I is the intermediate chlorosulfonium chloride written for the chlorination of phenyl methyl sulfide, and decomposes to III, which subsequently gives phenyl chloromethyl sulfide (IV).



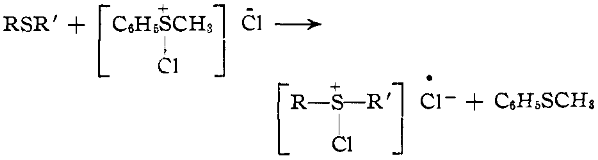
The reaction of phenyl methyl sulfoxide with carboxylic acid chlorides can give rise to an intermediate VI, comparable to V, and attack by chloride ion on sulfur can lead to displacement of $RCOO^-$ giving rise once more to the same cation as in I. Abstraction of a proton from the methyl group of this cation by $RCOO^-$ would give III, which would then give phenyl chloromethyl sulfide.

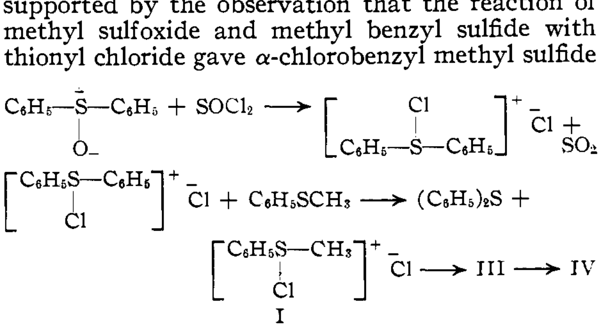


The sulfoxide rearrangements observed by Pummerer,[16] in which ethyl phenylsulfinylacetate reacts with hydrogen chloride to give ethyl α-phenylthio-α-chloroacetate or reacts with acetic anhydride to give ethyl α-phenylthio-α-acetoxyacetate also may be satisfactorily represented as involving sulfonium salt intermediates comparable to I, III, V and VI.



It would be anticipated that a sulfide could attack the positive chlorine of intermediate I (nucleophilic attack of sulfur on chlorine to displace sulfur). The postulate that intermediate I is present in the sulfoxide–thionyl chloride reaction was therefore supported by the observation that the reaction of methyl sulfoxide and methyl benzyl sulfide with thionyl chloride gave α-chlorobenzyl methyl sulfide





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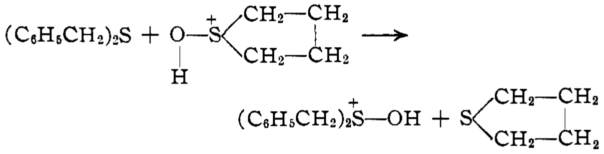
(14) A similar mechanism has been described previously (see refs. 5 and 6) in somewhat different terms. The low temperature halogenation of ethers in the absence of light may well follow a similar course, since halo oxonium halides have apparently been isolated at low temperatures (*e.g.*, see D. McIntosh, THIS JOURNAL, **32**, 1330 (1910)). Professor R. K. Summerbell has pointed out that the chlorination of 2-chlorodioxane to give 2,5-dichlorodioxane at low temperatures is consistent with the formation of a chloro-oxonium chloride at the more basic oxygen (see L. A. Bryan, W. M. Smedley and R. K. Summerbell, *ibid.*, **72**, 2206 (1950), **72**, 2206 (1950)), and he has been using this concept of the reaction.

(15) See R. Connor in the chapter, "Organic Sulfur Compounds," in "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., p. 872.

(16) R. Pummerer, *Ber.*, **43**, 1401 (1910).

as well as chloromethyl methyl sulfide. Similarly, a mixture of phenyl sulfoxide and methyl phenyl sulfide gave chloromethyl phenyl sulfide and phenyl sulfide.[17]

The success of these reactions prompted us to try an exchange of oxygen atom between a sulfide and a sulfoxide. No reaction between thiacyclopentane 1-oxide and benzyl sulfide was observed after refluxing in alcohol, benzene or acetic acid solution. However, in acetic acid containing a few drops of sulfuric acid the formation of some benzyl sulfoxide



was observed. This may be formulated as a nucleophilic displacement of sulfur on oxygen by sulfur.

Experimental[18]

Preparation of Sulfides.—The sulfides were for the most part prepared by methods that have been described previously.[19] Thiacyclobutane was obtained by the addition of 394 g. (2.5 moles) of 1-bromo-3-chloropropane during one hour to a heated and well-stirred solution of 228 g. (3.0 moles) of thiourea and 360 g. (9 moles) of sodium hydroxide in 1500 ml. of water. After two additional hours at reflux with vigorous stirring the mixture was steam distilled. After separation of the sulfide layer and drying over anhydrous potassium carbonate, distillation gave 84 g. (45% yield) of thiacyclobutane, b.p. 92–94°.[20]

p-Methoxyphenyl methyl sulfide was prepared by the convenient, but little used, reaction of the Grignard reagent with disulfides.[21,22] A solution of 66 g. (0.7 mole) of methyl disulfide in 200 ml. of ether was added slowly to the Grignard reagent prepared from 187 g. (1 mole) of *p*-bromoanisole and 32 g. (1.5 moles) of magnesium in 500 ml. of ether, giving rise to a moderately exothermic reaction and the appearance of a yellow precipitate. After standing overnight a solution of 180 ml. of concd. hydrochloric acid in 300 ml. of water was added slowly to the mixture (methyl mercaptan liberated). The ether extract was separated and dried over anhydrous sodium sulfate. Distillation gave 101 g. (93% based on methyl disulfide) of *p*-methoxyphenyl methyl sulfide, b.p. 98–100° (4 mm.). Suter and Hansen[23] report a b.p. of 99° (4 mm.).

Chlorination of Sulfides and Characterization of α-Chlorosulfides.—A solution of sulfuryl chloride (5% excess) in pentane (or methylene chloride) was added to a heated solution of the sulfide in pentane (or methylene chloride) during one or two hours. The mixture was heated an additional hour, allowed to stand, the major portion of the solvent removed at atmospheric pressure, and the residue distilled at reduced pressure through a 10-inch vacuum jacketed Vigreux column. In general, the b.p.'s of the α-chlorosulfides agreed with those reported by the previous investigators.[4-6]

Grignard Couplings.—The coupling reactions were brought about by adding the α-chlorosulfide in ether solution to about a 100% excess of phenylmagnesium bromide in ether. After standing overnight the mixture was hydrolyzed with water and the ether extract dried over anhydrous potassium carbonate and distilled.

The reaction with *t*-butylmagnesium chloride was abnormal. A solution of 39.6 g. (0.25 mole) of chloromethyl phenyl sulfide in 100 ml. of ether was added during 30 minutes to the Grignard reagent prepared from 47.5 g. (0.58 mole) of *t*-butyl chloride and 13 g. of magnesium in 300 ml. of ether. The mixture was heated for 30 minutes, the gas evolved being trapped in a Dry Ice trap containing pentane. Titration of the contents of the trap with bromine in carbon tetrachloride indicated the formation of 17% of isobutylene. After standing overnight the reaction mixture was processed in the usual manner to yield on distillation 9.5 g. (30%) of methyl phenyl sulfide, b.p. 82–84° (16 mm.), together with 5.2 g. of product, b.p. 121–123° (16 mm.), which was not characterized. The identity of the methyl phenyl sulfide was established by carrying out a mixed m.p. determination with the sulfone (m.p. 87.5–88°, prepared by oxidation) and an authentic sample.

Oxidation to Sulfones.—The sulfones were obtained by refluxing the sulfides for 15 minutes in an acetic acid solution containing about three times the theoretical quantity of 30% hydrogen peroxide and diluting the solution with water.

Chloromethyl Phenyl Sulfide.—Chlorination of methyl phenyl sulfide gave a 92% yield of material, b.p. 103–104° (12 mm.). Coupling with phenylmagnesium bromide gave 60% of phenyl benzyl sulfide, b.p. 171–193° (12 mm.), m.p. 43–44°. The sulfone obtained in 91% yield, melted at 143–144° and did not depress the m.p. of an authentic sample of phenyl benzyl sulfone.

α-Chlorobenzyl Phenyl Sulfide.—The chlorosulfide, b.p. 151–153° (2 mm.) (obtained in 65% yield), gave 60% of benzhydryl phenyl sulfide, m.p. 78–79°, in the coupling reaction with phenylmagnesium bromide. This product was identical with an authentic sample prepared by the reaction of benzhydrol and thiophenol in acetic acid solution in the presence of a drop of sulfuric acid. The sulfones, m.p. 187–188°, were also identical.

Carbethoxychloromethyl Carbethoxymethyl Sulfide.—From a chlorination carried out in methylene chloride solution, 70% of a product, b.p. 167–169° (20 mm.), was obtained.

Anal. Calcd. for $C_8H_{13}ClO_4S$: C, 39.92; H, 5.41. Found: C, 40.53; H, 5.45.

Chloromethyl *p*-Methoxyphenyl Sulfide.—Chlorination gave 79% of product, b.p. 144–146° (15 mm.).

Anal. Calcd. for C_8H_9ClOS: C, 50.93; H, 4.81. Found: C, 51.16; H, 4.75.

When treated with an aqueous alcoholic solution of silver nitrate the product immediately deposited a yellow precipitate of silver mercaptide, which is typical of an α-chlorosulfide. The chloromethyl *p*-methoxyphenyl sulfide decomposed to a brown tar after standing three weeks in a glass-stoppered bottle.

α-Chlorobenzyl Methyl Sulfide.—A 73% yield of chlorination product, b.p. 118–121° (14 mm.), was obtained as a straw-colored liquid which intensified in color to orange on standing. A 2.0-g. portion of the chlorosulfide was added to 15 ml. of a 40% acetic acid water solution containing 1.5 g. of phenylhydrazine; immediate crystallization took place. After recrystallization from alcohol the yield of benzaldehyde phenylhydrazone was 1.2 g. (53%).

Chloromethyl Methyl Sulfide.—The yield of chlorosulfide, b.p. 104–106°, was only about 40%, but some methyl sulfide was lost due to its volatility during the reaction. Coupling with phenylmagnesium bromide gave methyl benzyl sulfide, which was oxidized in 68% yield to methyl benzyl sulfone, m.p. and mixed m.p. with an authentic sample 125–126°.

A mixture of 16.2 g. (0.168 mole) of chloromethyl methyl sulfide and 35 g. (0.4 mole) of morpholine in 100 ml. of benzene was allowed to stand for 16 hours. The mixture was then added to a solution of 30 g. of potassium hydroxide in 300 ml. of water and ice. The benzene layer was separated and combined with a hexane wash. After drying over anhydrous potassium carbonate, distillation gave 15 g. (61%) of **N-(methylmercaptomethyl)-morpholine,** b.p. 94–100° (14 mm.).

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[17] Thionyl chloride has been shown to be a chlorinating agent for methyl sulfide (ref. 5). Reactions were found to occur also with methyl phenyl sulfide or methyl benzyl sulfide and thionyl chloride, but the α-chlorosulfides could not be isolated under conditions comparable to those used in these experiments.

[18] Microanalyses were carried out by Miss Joyce Sorenson and Miss Constance Brauer.

[19] See, *e.g.*, D. T. McAllan, T. V. Cullum and R. A. Dean, THIS JOURNAL, **73**, 3627 (1951), and E. V. Whitehead, R. A. Dean and F. A. Fidler, *ibid.*, **73**, 3632 (1951).

[20] R. W. Bost and R. W. Conn, *Oil Gas J.*, **32** [3], 17 (1933), report a 30% yield from 1,3-dichloropropane and sodium sulfide. Stewart and Burnside[11] obtained a 45% yield from 1,3-dibromopropane and sodium sulfide.

[21] H. Wuyts, *Bull. soc. chim.*, [3] **35**, 166 (1906).

[22] The experiment described was performed by Pierre Boutan.

[23] C. M. Suter and H. L. Hansen, THIS JOURNAL, **54**, 4100 (1932).

Anal. Calcd. for $C_6H_{13}NOS$: C, 48.94; H, 8.90; N, 9.52. Found: C, 49.18; H, 8.89; N, 10.11, 10.00.

The picrate was obtained by addition of the aminosulfide to a solution of picric acid in acetone; m.p. 140° dec. After crystallization from acetone–alcohol the decomposition point remained essentially unchanged.

Anal. Calcd. for $C_{12}H_{16}N_4O_8S$: C, 38.29; H, 4.29; N, 14.89. Found: C, 38.89; H, 4.48; N, 15.06.

The aminosulfide reacted vigorously with hydrogen peroxide, but no distinct product was obtained.

α-Chloroethyl Ethyl Sulfide.—A 75% yield of α-chlorosulfide, b.p. 30–31° (11 mm.), was obtained by chlorination; within three days the material had turned to a black sirup. An 80% yield of ethyl α-phenylethyl sulfide, b.p. 92–93° (8 mm.), was obtained by coupling with phenylmagnesium bromide. The sulfone and sulfilimine corresponding to this sulfide were oils. Attempts to obtain solid derivatives of ethyl *s*-butyl sulfide, b.p. 130–131°, prepared in 51% yield by coupling α-chloroethyl ethyl sulfide with ethylmagnesium bromide, also were unsuccessful.

Chloromethyl *t*-Butyl Sulfide.—Distillation of the chlorination mixture gave a yellow product, b.p. 60–65° (20 mm.). Redistillation gave 40% of product, b.p. 65–67° (28 mm.). Coupling with phenylmagnesium bromide gave 59% of benzyl *t*-butyl sulfide, b.p. 129–131° (21 mm.). Oxidation gave 70% of **benzyl *t*-butyl sulfone**, m.p. 126–127°.

Anal. Calcd. for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60. Found: C, 62.30; H, 7.66.

Thiacyclopentane.—Under the usual chlorination conditions with sulfuryl chloride, thiacyclopentane gave resinous material together with small quantities of lower boiling products having a wide b.p. range. From one experiment, where addition of a 2 molar quantity of chlorine at low temperature was followed by an atmospheric distillation and finally a vacuum distillation, a small distillation cut was isolated, which is believed to contain 2,3-dichlorothiacyclopentane, since coupling with phenylmagnesium bromide and oxidation gave a sulfone, m.p. 154–155°, whose analysis was consistent with that of a chlorothiacyclopentane 1,1-dioxide.

Anal. Calcd. for $C_{10}H_{11}ClO_2S$: C, 52.06; H, 4.81. Found: C, 52.03; H, 4.88.

Thiacyclohexane.—The reaction of thiacyclohexane with sulfuryl chloride at 35° did not produce resinous products, as was true of thiacyclopentane; a considerable part of the material was contained in a low boiling forerun. In one experiment 34 g. (0.25 mole) of sulfuryl chloride in 50 ml. of pentane was added to 25.5 g. (0.25 mole) of thiacyclohexane in 50 ml. of pentane at 0–5°. The crystalline chlorine addition compound separated at first, but gradually changed to an oil. The mixture was gradually warmed and then heated at reflux for one-half hour. The solvent was removed and the residue distilled yielding 12 g. of product, b.p. 39–40° (17 mm.), and a further cut distilling at 45–110° (authentic thiacyclohexane boiled at 39–40° under these conditions). Redistillation of the 39–40° material at atmospheric pressure gave 6 g. of product, b.p. 137–139°, n^{20}_D 1.5328.[24] The proportion of 2-thiacyclohexene was 28%, judging from the refractive index and assuming a binary mixture. Two grams of the mixture was treated with 2.0 g. of thiophenol in 10 ml. of acetic acid, and 3 drops of sulfuric acid was added. After standing for a short while the mixture was diluted with water, extracted with ether and washed with 10% sodium hydroxide. Concentration of the ether extract gave a residue which was oxidized with 5 ml. of 30% hydrogen peroxide in 25 ml. of acetic acid at reflux for 20 minutes. On dilution with water, 1.0 g. of sulfone, presumably **2-phenylsulfonylthiacyclohexane 1,1-dioxide**, m.p. 142–143°, was obtained. The sulfone was recrystallized from alcohol; m.p. 142.5–143°. The yield of sulfone corresponds to the presence of 18% of 2-thiacyclohexene in the mixture.

Anal. Calcd. for $C_{11}H_{14}O_4S_2$: C, 48.15; H, 5.14. Found: C, 48.26; H, 5.27.

γ-Chloropropanesulfenyl Chloride.—A heated solution of 27 g. (0.36 mole) of thiacyclobutane in 80 ml. of pentane containing a crystal of iodine was treated with a solution of 50 g. (0.37 mole) of sulfuryl chloride in 60 ml. of pentane. After approximately half the sulfuryl chloride was added, the mixture gradually developed a bright yellow color. After an additional hour at reflux the mixture was distilled to give 36.5 g. (69%) of a yellow orange liquid, b.p. 64–66° (13 mm.).[9] On standing the sulfenyl chloride rapidly darkened to a black tar with the evolution of hydrogen chloride.

Reaction of *p*-Tolyl and Phenyl Chloromethyl Sulfides with Magnesium.—Addition of 2.4 g. of *p*-tolyl chloromethyl sulfide in 20 ml. of dry ether to 1 g. of magnesium and a crystal of iodine resulted in a rapid exothermic reaction. The mixture was maintained at reflux for one hour and hydrolyzed with dilute hydrochloric acid. The ether layer was dried over anhydrous potassium carbonate, the ether evaporated and the product crystallized from hexane. In this manner 0.5 g. (26%) of 1,2-bis-(*p*-tolylmercapto)-ethane, m.p. 78–79°, was obtained. Bell and Bennett[25] report a m.p. of 81°. Oxidation of 0.2 g. with 30% hydrogen peroxide in acetic acid gave the sulfone, m.p. 199–200°; Otto[26] gives a m.p. of 199.5–200.5°. 1-Bis-(phenylmercapto)-ethane, m.p. 68–69° (Bell and Bennett[25] report m.p. 69°) was obtained in a similar manner by the reaction of phenyl chloromethyl sulfide and magnesium. The sulfone obtained on oxidation melted at 180–181° (Otto[26] reported a m.p. of 179.5–180°).

When similarly treated with magnesium, chloromethyl methyl sulfide, chloromethyl *t*-butyl sulfide and α-chlorobenzyl methyl sulfide failed to show any reaction.

Preparation of Sulfoxides.—The method was that of Hinsberg[27] using an equimolar portion of 30% hydrogen peroxide in acetone or acetic acid as the solvent. Tests were made for peroxide with starch–iodide paper prior to distillation. An explosion occurred in an attempted preparation of allyl sulfoxide. The procedure for benzyl methyl sulfoxide is representative.

Benzyl Methyl Sulfoxide.—Twenty-five ml. of 30% hydrogen peroxide (0.25 mole) was added during one-half hour in 5-ml. portions to a solution of 35 g. (0.25 mole) of benzyl methyl sulfide in 100 ml. of acetic acid with occasional cooling to keep the temperature below 50°. After 24 hours the solution was poured into a solution of 80 g. of sodium hydroxide in 500 ml. of water. The sulfoxide was extracted with ether, the ether layer was dried over anhydrous potassium carbonate and distilled, yielding 37 g. (94%) of methyl benzyl sulfoxide, b.p. 116–118° (0.8 mm.).

Anal. Calcd. for $C_8H_{10}OS$: C, 62.30; H, 6.54. Found: C, 62.51; H, 6.80.

***p*-Chlorophenyl methyl sulfoxide**, b.p. 142–144° (6 mm.), was prepared in 88% yield by a similar procedure.

Anal. Calcd. for C_7H_7ClOS: C, 48.14; H, 3.99. Found: C, 48.24; H, 4.16.

The Reaction of Sulfoxides and Thionyl Chloride.—In general, the sulfoxide was dissolved in methylene chloride and added slowly to a heated solution of methylene chloride containing about 95% excess of the theoretical quantity of thionyl chloride. The reaction mixture was then heated at the reflux point for an additional hour, or allowed to stand overnight at room temperature and distilled. A typical procedure is as follows. A solution of 28 g. (0.20 mole) of methyl phenyl sulfoxide in 40 ml. of methylene chloride was added during 2 hours to a heated solution of 27 g. (0.23 mole) of thionyl chloride in 40 ml. of methylene chloride. The solution was refluxed for an additional hour and distilled giving 29.3 g. (92%) of chloromethyl phenyl sulfide, b.p. 99–101° (7 mm.). The b.p.'s and yields of other α-chloro sulfides prepared from sulfoxides were as follows: chloromethyl methyl sulfide, b.p. 104–106° (92%); α-chloroethyl ethyl sulfide, b.p. 45–48° (45 mm.) (40%); chloromethyl *p*-chlorophenyl sulfide, b.p. 112–114° (6 mm.) (90%); α-chlorobenzyl methyl sulfide, b.p. 109–111° (8 mm.) (75%); chloromethyl *t*-butyl sulfide, b.p. 66–70° (35 mm.) (39%). Thiacyclopentane 1-oxide with thionyl chloride gave a dark colored material with a wide boiling range; the results are similar to those obtained with thiacyclopentane and sulfuryl chloride.

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[24] Y. K. Yur'ev, T. B. Dubrovina and E. P. Tregubor, *J. Gen. Chem.* (*U.S.S.R*), **16**, 843 (1946); *C. A.*, **41**, 1654 (1947).

[25] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 3189 (1928).

[26] R. Otto, *Ber.*, **13**, 1272 (1880).

[27] (a) O. Hinsberg, *ibid.*, **41**, 2836 (1908); (b) see also D. S. Tarbell and C. Weaver, THIS JOURNAL, **63**, 2939 (1941), and ref. cited therein.

Phenyl Vinyl Sulfide.—A solution of 40 g. (0.26 mole) of ethyl phenyl sulfoxide in 40 ml. of methylene chloride was added to a heated solution of 34 g. (0.28 mole) of thionyl chloride in 40 ml. of methylene chloride during 2.5 hours. The solvent was distilled off, first at atmospheric pressure and finally with the aid of an aspirator. Distillation of the residue gave 11 g. (31%) yield of phenyl vinyl sulfide, b.p. 72–75° (6 mm.).

In a comparable experiment using 0.15 mole of ethyl phenyl sulfoxide, the residue was heated with 75 ml. of pyridine at the reflux point for 30 minutes, diluted with 300 ml. of water and steam distilled. Extraction of the distillate with ether, drying the ether extract over potassium carbonate and distillation gave 13.3 g. (65%) of phenyl vinyl sulfide, b.p. 77–78° (12 mm.). Oxidation of a sample with hydrogen peroxide in acetic acid gave a 60% yield of phenyl vinyl sulfone, m.p. and mixed m.p. with an authentic sample, 66–67°. Phenyl vinyl sulfide became colored yellow within 24 hours and after one week turned to a black sirup.

The Reaction of Methyl Sulfoxide with Methyl Benzyl Sulfide and Thionyl Chloride.—A solution of 15.6 g. (0.20 mole) of methyl sulfoxide and 27.6 g. (0.20 mole) of benzyl methyl sulfide in 50 ml. of methylene chloride was added to a heated solution of 26.4 g. (0.22 mole) of thionyl chloride in 40 ml. of methylene chloride during 90 minutes. The mixture was distilled, first at atmospheric pressure to yield 8.0 g. (41%) of chloromethyl methyl sulfide, b.p. 104–106°, and then under vacuum giving 12 g. (35%) of α-chlorobenzyl methyl sulfide, b.p. 125–130° (15 mm.).

Methyl benzyl sulfide when treated alone with thionyl chloride in the above manner gave no sharp boiling product.

The Reaction of Phenyl Sulfoxide with Methyl Phenyl Sulfide and Thionyl Chloride.—When the reaction was carried out essentially in the manner used for methyl sulfoxide and methyl benzyl sulfide, 58% of chloromethyl phenyl sulfide, b.p. 78–80° (2 mm.) and 65% of phenyl sulfide, b.p. 115–116° (2 mm.) were obtained. The chloromethyl phenyl sulfide was identified by oxidation to the sulfone, m.p. 52–53°, using 40% peracetic acid.[7] The phenyl sulfide was characterized by way of the sulfilimine, m.p. 109–110°. Tarbell and Weaver[25b] report m.p. 108–110°.

The Reaction of Benzyl Sulfide and Thiacyclopentane 1-Oxide.—No reaction was observable between benzyl sulfide and thiacyclopentane 1-oxide after 16 hours reflux in alcohol solution in the presence or absence of potassium hydroxide. Benzyl sulfide was also recovered after refluxing in benzene solution with methyl sulfoxide (6 hours) or thiacyclopentane 1-oxide (16 hours). However, during 16 hours reflux of 2.14 g. (0.01 mole) of benzyl sulfide and 4.16 g. (0.04 mole) of thiacyclopentane 1-oxide in 25 ml. of acetic acid containing 5 drops of sulfuric acid a black tarry mixture was formed. The mixture was diluted with water and extracted with 200 ml. of ether and the ether layer was washed three times with 100 ml. of water and then diluted with alcohol. After removal of the ether (steam-bath) and treatment with charcoal, concentration of the solution under reduced pressure gave 0.40 g. (17%) of benzyl sulfoxide, m.p. 131–133°. The m.p. after crystallization from benzene–hexane was 133–134° and was not depressed by an authentic sample.

The Reaction of Sulfoxides with Acid Halides.—A solution of 5.6 g. (0.04 mole) of methyl phenyl sulfoxide in 20 ml. of benzene was added to a refluxing solution of 7.5 g. (0.04 mole) of *p*-nitrobenzoyl chloride in 75 ml. of benzene during 15 minutes and the reaction was further heated at reflux for 30 minutes. During the reaction some hydrogen chloride was evolved. Filtration and further concentration yielded in all 6.6 g. (98%) of *p*-nitrobenzoic acid. The concentrate was added to a solution of 11 g. (0.1 mole) of thiophenol in 100 ml. of ethanol containing 7 g. of potassium hydroxide, and this mixture was heated at reflux for one hour. The major portion of the solvent was then distilled off and the residue was poured into water and extracted with ether. The ether layer was washed with 10% potassium hydroxide and dried over anhydrous potassium carbonate. The dried extract was concentrated on a steam-bath to 30 ml. and a 2.5-ml. aliquot was oxidized with 5 ml. of 30% hydrogen peroxide. Dilution with water gave 1.9 g. (64%) of bis-(phenylsulfonyl)-methane, m.p. 117–119°. Recrystallization from alcohol gave material, m.p. 119–120°, which gave no m.p. depression when mixed with an authentic sample. From the remainder of the ether solution bis-(phenylmercapto)-methane was obtained; recrystallization from ether–pentane gave material, m.p. 34–35°, as compared to a literature value of 35–36°.[28]

In similar experiments with methyl benzyl sulfoxide and thiacyclopentane 1-oxide 94% and 48% yields of *p*-nitrobenzoic acid were obtained. Resinous material was formed in the latter case.

A solution of 11.7 g. (0.15 mole) of methyl sulfoxide in 30 ml. of methylene chloride was added during 30 minutes to a refluxing solution of 45 g. (0.32 mole) of benzoyl chloride in 50 ml. of methylene chloride. The mixture was heated an additional hour and then distilled to yield chloromethyl methyl sulfide, b.p. 103–108°; redistillation gave 7 g. (45%) of material, b.p. 104–106°.

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(28) R. L. Shriner, W. J. Struck and H. C. Jorison, This Journal, **52**, 2060 (1930).

Evanston, Illinois

[Contribution from Eaton Laboratories, Division of The Norwich Pharmacal Company]

4-Nitro-2-thenaldehyde. II

By Gabriel Gever

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Previously reported 4-nitro-2-thenaldehyde and its diacetate have been shown to have consisted of mixtures of the 4- and 5-nitro isomers. Pure 4-nitro-2-thenaldehyde and its diacetate have been prepared and characterized.

In a previous publication[1] it was reported that the nitration of 2-thenaldehyde diacetate with acetic anhydride–nitric acid gave a small amount of 4-nitro-2-thenaldehyde diacetate in addition to the main product, 5-nitro-2-thenaldehyde diacetate. The 4-nitro-2-thenaldehyde diacetate was converted to 4-nitro-2-thenaldehyde. Subsequently, Foye[2] nitrated 2-thenaldehyde with a mixture of sulfuric acid and fuming nitric acid to obtain a 64.5% yield of 4-nitro-2-thenaldehyde, no 5-nitro-2-thenaldehyde being obtained.

In view of the known propensity of thiophenes to substitute in the 5-position,[3] reinvestigation of 4-nitro-2-thenaldehyde and its diacetate was instituted. Rinkes[4] had shown that one of the products of the nitration of methyl 2-thienyl ketone, previously reported as pure methyl 5-nitro-2-thienyl ketone was, in reality, a mixture of methyl 4-nitro-2-thienyl ketone and methyl 5-nitro-2-thienyl ketone. It has now been found that the 4-nitro-2-thenaldehyde reported earlier[1,2] is actu-

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(1) G. Gever, This Journal, **75**, 4585 (1953).

(2) W. Foye, J. Hefferren and E. Feldmann, *ibid.*, **76**, 1378 (1954).

(3) H. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., pp. 147, 225.

(4) I. Rinkes, *Rec. trav. chim.*, [4] **52**, 538 (1933).