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THE OXIDATION OF PROPYLENE SULFIDE

by

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B.A., Montana State University, 1949

Presented in partial fulfillment of the
requirement for the degree of
Master of Science

Montana State University

1951

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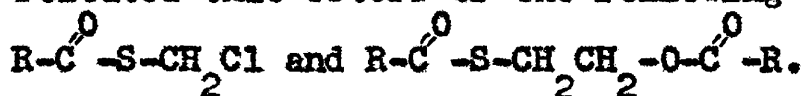
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CHAPTER I

INTRODUCTION

Reactions of olefin sulfides heretofore reported have produced mercaptans or derivatives of mercaptans. The sulfide ring has been opened by reaction with labile hydrogen containing compounds such as organic acids, hydrochloric acid,¹ amines,² alcohols³ and mercaptans,^{3,4} giving respectively the following types of substituted mercaptans: acyloxy mercaptans, chloromercaptans, aminomercaptans, alkoxy mercaptans and thio mercaptans. Acylations have been accomplished with acetyl chloride,⁵ acetyl bromide, acetic anhydride¹ and benzoyl chloride,⁵ giving substituted thio esters of the following types:



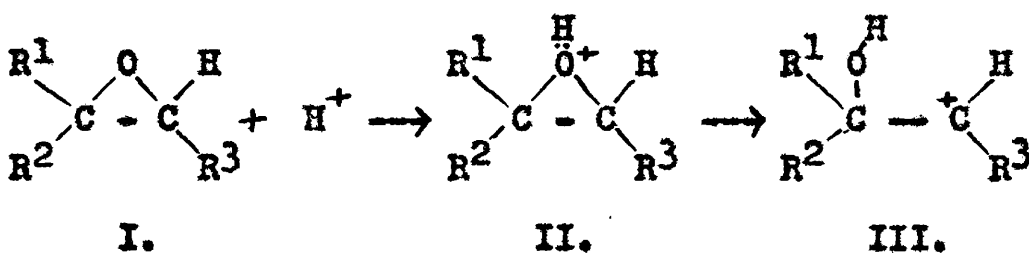
The olefin sulfides polymerize much more readily than the analogous olefin oxides. Among reagents causing rapid polymerization are: Traces of acids or bases, metalloids halides such as boron trifluoride, hydrazine and hydroxylamine.

Reactions of unsymmetrically substituted ethylene oxides usually open the epoxide ring with the oxygen atom remaining on the most highly substituted carbon atom. In the cleavage of substituted ethylene oxides, the terms normal cleavage and abnormal cleavage have been applied. These terms have carried over into

discussions of the cleavage of the olefin sulfides. The opening of the epoxide ring to form secondary alcohol is considered to be the normal reaction, and the formation of primary alcohols, the abnormal.^{6,7,8}

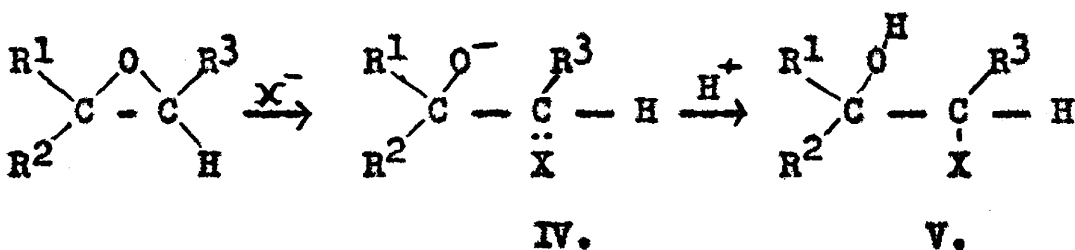
The mechanism of the cleavage of the epoxide has been postulated to take place in the following manner:

Acid catalyzed:



The mechanism involving the unimolecular ring opening of the oxide-conjugate acid II is followed by the rapid reaction of the open carbonium ion, III, with an anion.^{6,9}

Base catalyzed:



In basic media the mechanism is postulated as involving a nucleophilic attack by an anion (X^-) on the more positive carbon of the epoxide ring, giving cleavage of the oxide linkage at this point and an intermediate IV is produced. This then reacts rapidly with a proton to form V.

These mechanisms indicate that the preponderance of epoxide cleavages should occur in the normal manner. The ethylene sulfide series is not as consistent, as reactions have been reported where the products were mainly normal, other reactions where the products were mainly abnormal, and still others where mixtures of isomers in various ratios were apparently obtained.

Reactions of ethylene sulfides with amines have been reported to yield mainly amino mercaptans in which the sulfur atom remains on the more highly substituted carbon,² a normal cleavage. Aqueous HCl and ethylene sulfides are reported to proceed by abnormal cleavage in forming chloromercaptans.¹ Mercaptans when reacted with ethylene sulfides usually yield mixtures of isomeric thiomercaptans, with neither the abnormal nor the normal reaction predominating throughout the series.³ Alcohols have been reported to yield products resulting from the abnormal cleavage.³ Acylation reactions proceed both normally and abnormally. Acetic anhydride in pyridine gives the normal ring opening, while the acyl halides, acetyl chloride, acetyl bromide, and benzoyl chloride, give the abnormal ring opening.¹

CHAPTER II

STATEMENT OF THE PROBLEM

There have been two main objectives in this work. One has been the study of the oxidation of propylene sulfide with various oxidizing agents and identification of the types of products obtained. The second has been the proof of structure of the products; i.e., the direction of cleavage of the olefin sulfide ring under the influence of the oxidizing agents used.

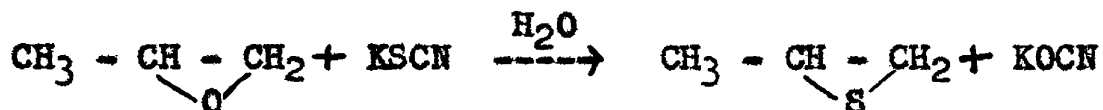
The sulfur atom in the olefin sulfide ring system has been shown to be incapable of expanding its valence shell without cleavage of the ring taking place.⁵ Propylene sulfide, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{S}$, is an asymmetrically substituted ethylene sulfide derivative. When this ring is opened, the sulfur atom in the derivative formed will remain attached either to a secondary carbon atom, or to a primary carbon atom.

The compounds which were formed in these oxidations of propylene sulfide have been mentioned briefly, if at all, in previous literature, and solid derivatives apparently have not been made previously. Therefore, it was necessary to resort to other unequivocal methods of synthesis of these compounds, giving known structures. The two series could then be compared through physical constants and through solid derivatives of definite melting point.

CHAPTER III

DISCUSSION OF WORK

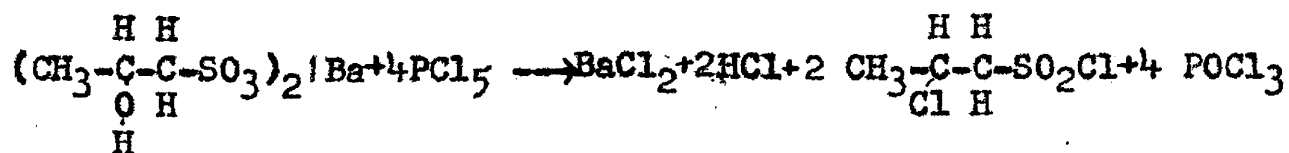
The propylene sulfide used in these experiments was prepared by a reaction between propylene oxide and potassium thiocyanate.^{2,10,11}



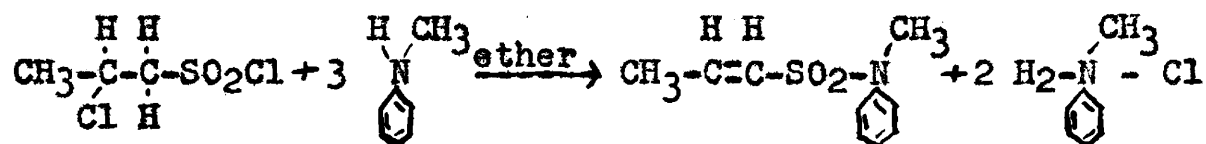
The oxidizing agents used in this study were 30% hydrogen peroxide solution, 69% nitric acid, and chlorine water.

With 30% hydrogen peroxide solution as oxidizing agent, the products containing sulfur have been identified as sulfuric acid (from complete cleavage of the sulfur atom from the original material), and a β -hydroxypropane sulfonic acid. An aliquot portion of the oxidized material was taken for analysis for total acid and sulfate. Conversion of the acid products to barium salts allowed the soluble barium hydroxypropane sulfonate to be separated from the sulfate. The barium hydroxypropane sulfonate was then converted to the free sulfonic acid, from which the phenylhydrazine salt was made as a solid derivative.¹²

The barium β -hydroxypropane sulfonate was reacted with phosphorus pentachloride to yield a β -chloropropane sulfonyl chloride. Structure used in these equations is the isomer proven correct by subsequent work.

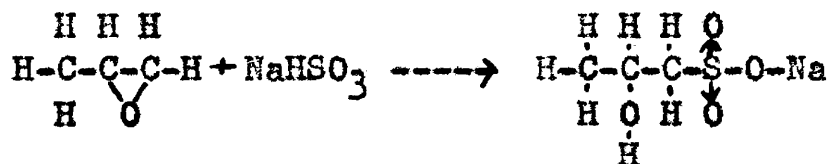


The methyl anilide of this chloropropane sulfonyl chloride was prepared, and melted at 56-57.5°C. This derivative contained no halogen and analysis showed it to be an unsaturated methyl anilide of structure shown in the following equation:



This type of reaction has been reported previously.¹³

As a reference compound, sodium 2-hydroxypropane-1-sulfonate was prepared by the reaction of sodium bisulfite with propylene oxide.¹⁴



This reaction has been shown to give the secondary alcohol formation. The β -hydroxypropane sulfonate was converted to 2-chloropropane-1-sulfonyl chloride with PCl_5 . The chloro-sulfonyl chloride was then converted into a methyl aniline derivative. This compound had a melting point of 57-58°C. and showed no depression of melting point upon being admixed with the derivative prepared from the chloropropane sulfonyl chloride from the peroxide oxidation. The two chloropropane sulfonyl chlorides thus appear to be identical.

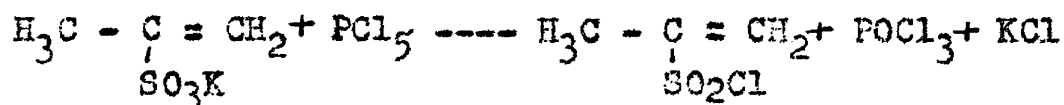
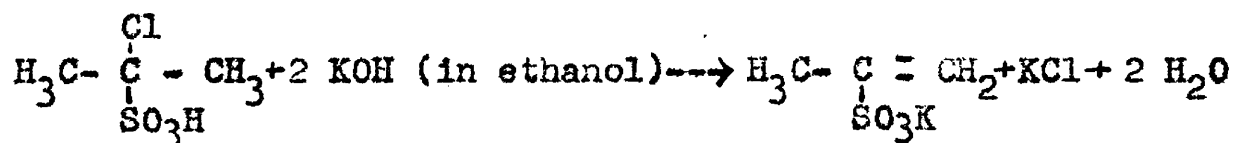
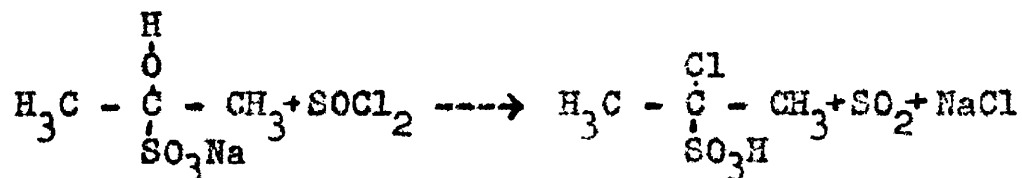
Oxidation with 69% nitric acid appeared to give results identical to those obtained with peroxide.

Propylene sulfide was oxidized directly with chlorine and water by adding the sulfide to water into which chlorine was being passed. An oily product isolated in good yield proved to be a β -chloropropane sulfonyl chloride. The stability of this sulfonyl chloride toward water is such that hydrolysis with water is accomplished only by long standing or refluxing, and hydrolysis apparently is accompanied by removal of the chloride group as HCl. The boiling point of this chloropropane sulfonyl chloride agrees with the sulfonyl chloride prepared from phosphorus pentachloride treatment of the peroxide oxidation product, 2-hydroxypropane sulfonic acid, but the refractive indexes do not agree. The melting point of the methyl aniline derivative does not agree. Considerable depression is given by a mixed melting point of these two derivatives. Therefore, it can be concluded that this oxidation product is 1-chloropropane-2-sulfonyl chloride.

2-Chloropropane-1-thiol was prepared according to the method of Davies and Savige,¹ by adding propylene sulfide to concentrated hydrochloric acid in methanol. These investigators have apparently proved the addition of HCl to be "abnormal", and to give the primary thiol. The purified product was oxidized with chlorine and water to give 2-chloropropane-1-sulfonyl chloride. Refractive

index and boiling point of the chloro-sulfonyl chloride agree with those of the chloro-sulfonyl chloride of the peroxide oxidation product. The melting point of the methyl aniline derivative agrees with that of the chloro-sulfonyl chloride of the peroxide oxidation product, and the chloro-sulfonyl chloride of the bisulfite-propylene oxide addition product. A mixed melting point of either of these pairs shows no depression. These results, then, agree with those of Davies and Savige, in showing the opening of the propylene sulfide ring by hydrochloric acid to be "abnormal".

Sodium-2-hydroxypropane-2-sulfonate was prepared by the addition of sodium bisulfite to acetone.¹⁵ Attempts were made to convert the sodium salt directly to 2-chloropropane-2-sulfonyl chloride through the use of PCl_5 , PCl_3 , and POCl_3 , but only a black product was obtained which could not be distilled. Therefore, it was decided to do this conversion in stages, as follows:



The unsaturated sulfonyl chloride was not successfully prepared.

Attempts were made to prepare other solid derivatives. From the salts of the sulfonic acids acidified with HCl, attempts were made to prepare derivative salts with piperidine, pyridine, and p-toluidine. The melting points of these salts were too indefinite to be useful in comparison studies.

Attempts to convert the chloropropane sulfonyl chlorides to solid sulfonamides with ammonium hydroxide, aniline, p-toluidine, dibenzylamine and dimethyl amine hydrochloride and NaHCO_3 were all unsuccessful, only oils which could not be made to crystallize being obtained. An attempt to prepare an ester with benzyl alcohol was a failure.

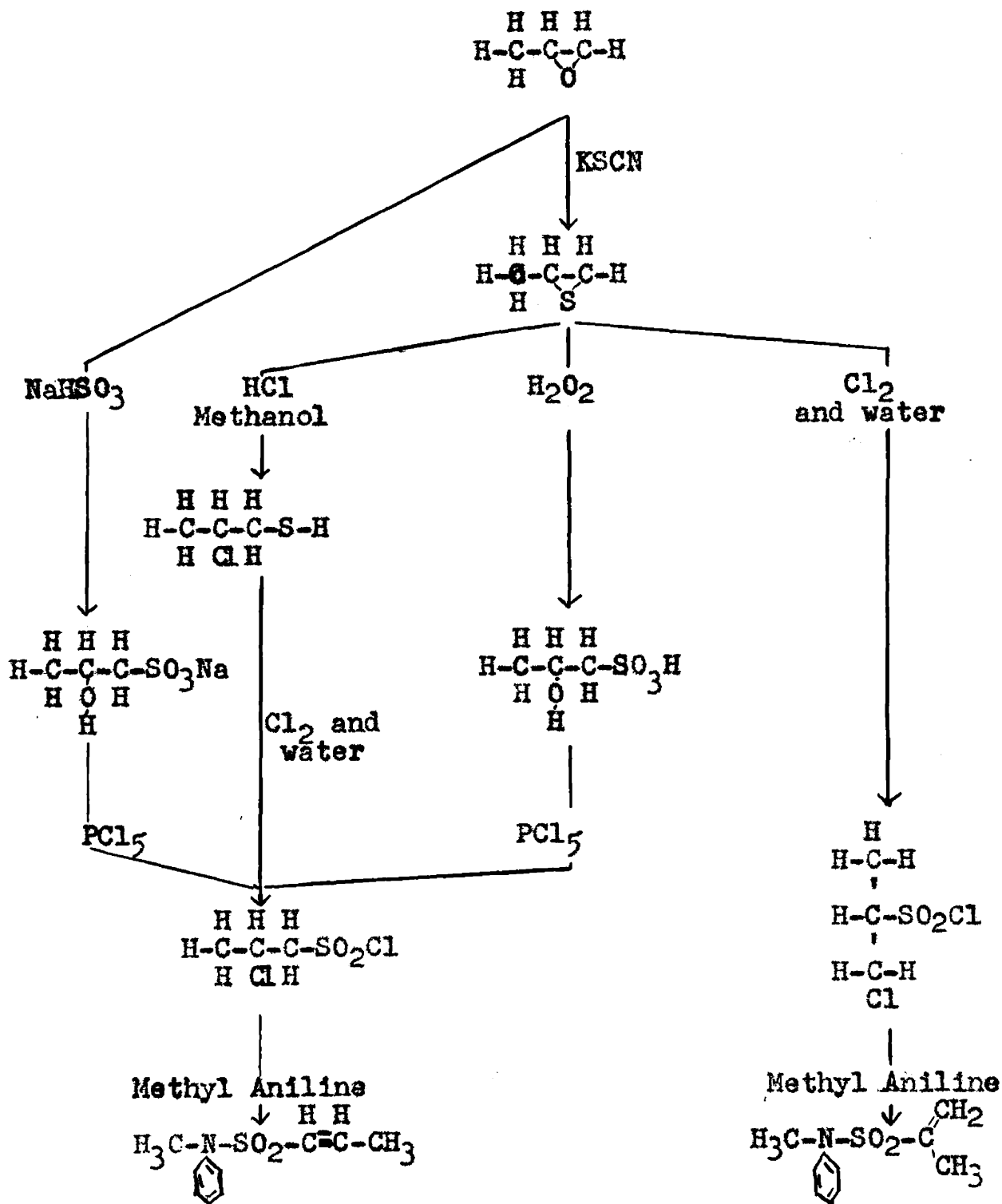


TABLE I
SUMMARY OF REACTION TIMES AND TEMPERATURES
30% H₂O₂ Oxidation

Addition		Reaction		Acid as 1.0 N.		Ratio
Time	Temp.		Temp.	Total Acid cc.	Sulfate cc.	Total acid: Sulfate
30	ice-water		ice-water	45.45	28.68	1.7:1
35	ice-water	3 hrs.	ice-water	58.48	19.4	3:1
45	ice-water	1 hr.	40°C.	88.32	34.99	2.5:1
65	ice-water	1 hr.	75-80°C.	121.05	41.40	2.9:1
45	20°C.	2 hrs.	20°C.	129.16	41.70	3.1:1
55	35-40°C.	1 hr.	40°C.	140.53	56.63	2.5:1
50	40°C.	2 hrs.	40°C.	126.22	40.15	3.1:1 *
55	40°C.	1 hr.	80°C.	154.52	55.03	2.8:1

The amount of propylene sulfide used in these oxidations was 7.4 grams (0.1 moles). Hydrogen peroxide was used in an amount of 45.5 grams (0.4 moles).

The above titrations were conducted with a Beckman pH meter. No evidence of a secondary ionization could be found when these titrations were graphed.

* This oxidation is the one given in the graph.

TABLE II
SUMMARY OF PHYSICAL CONSTANTS

SOURCE	CHLOROPROPANE SULFONYL CHLORIDE		MELTING POINT Methyl aniline derivative
	Boiling point	Refractive index	
1. H_2O_2 oxidized	57-55°C/1 mm.	n_D^{20} 1.4835	56-57.5°C
2. Cl_2 - H_2O oxidized propylene sulfide	55-56°C/1 mm. 77-79°C/8 mm.	n_D^{20} 1.4859	53.5-54.5°C
3. Propylene sulfide HCl in methanol Cl_2 - H_2O oxidized	51°C/1 mm.	n_D^{20} 1.4832	56.8-57.8°C
4. Propylene oxide sodium bisulfite PCl_5	51-52°C/1 mm.	n_D^{20} 1.4820	57.2-58.2°C

Mixed melting points

1 and 2 All melted below 50°C.

1 and 3 No depression of melting point.

1 and 4 No depression of melting point.

Titration of H_2O_2 Oxidation

Base: $0.1N\ NaOH$

cc	pH	cc	pH	cc
0.00	2.48	77.00	3.05	10.00
1.00	2.48	73.00	3.07	11.90
2.00	2.46	73.00	3.10	11.50
3.00	2.47	75.30	3.15	12.00
4.00	2.45	74.00	3.19	12.50
5.00	2.43	77.00	3.21	13.00
6.00	2.42	78.00	3.24	13.50
7.00	2.41	79.00	3.27	14.00
8.00	2.40	80.00	3.30	14.50
9.00	2.39	81.00	3.32	14.90
10.00	2.38	82.00	3.33	15.30
11.00	2.37	83.00	3.34	15.70
12.00	2.36	84.00	3.35	16.10
13.00	2.35	85.00	3.36	16.50
14.00	2.34	86.00	3.37	16.90
15.00	2.33	87.00	3.37	17.30
16.00	2.32	88.00	3.38	17.70
17.00	2.31	89.00	3.38	18.10
18.00	2.30	90.00	3.39	18.50
19.00	2.29	91.00	3.39	18.90
20.00	2.28	92.00	3.39	19.30
21.00	2.27	93.00	3.39	19.70
22.00	2.26	94.00	3.39	20.10
23.00	2.25	95.00	3.39	20.50
24.00	2.24	96.00	3.39	20.90
25.00	2.23	97.00	3.39	21.30
26.00	2.22	98.00	3.39	21.70
27.00	2.21	99.00	3.39	22.10
28.00	2.20	100.00	3.39	22.50
29.00	2.19			22.90
30.00	2.18			23.30
31.00	2.17			23.70
32.00	2.16			24.10
33.00	2.15			24.50
34.00	2.14			24.90
35.00	2.13			25.30
36.00	2.12			25.70
37.00	2.11			26.10
38.00	2.10			26.50
39.00	2.09			26.90
40.00	2.08			27.30
41.00	2.07			27.70
42.00	2.06			28.10
43.00	2.05			28.50
44.00	2.04			28.90
45.00	2.03			29.30
46.00	2.02			29.70
47.00	2.01			30.10
48.00	2.00			30.50
49.00	1.99			30.90
50.00	1.98			31.30
51.00	1.97			31.70
52.00	1.96			32.10
53.00	1.95			32.50
54.00	1.94			32.90
55.00	1.93			33.30
56.00	1.92			33.70
57.00	1.91			34.10
58.00	1.90			34.50
59.00	1.89			34.90
60.00	1.88			35.30
61.00	1.87			35.70
62.00	1.86			36.10
63.00	1.85			36.50
64.00	1.84			36.90
65.00	1.83			37.30
66.00	1.82			37.70
67.00	1.81			38.10
68.00	1.80			38.50
69.00	1.79			38.90
70.00	1.78			39.30
71.00	1.77			39.70
72.00	1.76			40.10
73.00	1.75			40.50
74.00	1.74			40.90
75.00	1.73			41.30
76.00	1.72			41.70
77.00	1.71			42.10
78.00	1.70			42.50
79.00	1.69			42.90
80.00	1.68			43.30
81.00	1.67			43.70
82.00	1.66			44.10
83.00	1.65			44.50
84.00	1.64			44.90
85.00	1.63			45.30
86.00	1.62			45.70
87.00	1.61			46.10
88.00	1.60			46.50
89.00	1.59			46.90
90.00	1.58			47.30
91.00	1.57			47.70
92.00	1.56			48.10
93.00	1.55			48.50
94.00	1.54			48.90
95.00	1.53			49.30
96.00	1.52			49.70
97.00	1.51			50.10
98.00	1.50			50.50
99.00	1.49			50.90
100.00	1.48			51.30
101.00	1.47			51.70
102.00	1.46			52.10
103.00	1.45			52.50
104.00	1.44			52.90
105.00	1.43			53.30
106.00	1.42			53.70
107.00	1.41			54.10
108.00	1.40			54.50
109.00	1.39			54.90
110.00	1.38			55.30
111.00	1.37			55.70
112.00	1.36			56.10
113.00	1.35			56.50
114.00	1.34			56.90
115.00	1.33			57.30
116.00	1.32			57.70
117.00	1.31			58.10
118.00	1.30			58.50
119.00	1.29			58.90
120.00	1.28			59.30
121.00	1.27			59.70
122.00	1.26			60.10
123.00	1.25			60.50
124.00	1.24			60.90
125.00	1.23			61.30
126.00	1.22			61.70
127.00	1.21			62.10
128.00	1.20			62.50
129.00	1.19			62.90
130.00	1.18			63.30
131.00	1.17			63.70
132.00	1.16			64.10
133.00	1.15			64.50
134.00	1.14			64.90
135.00	1.13			65.30
136.00	1.12			65.70
137.00	1.11			66.10
138.00	1.10			66.50
139.00	1.09			66.90
140.00	1.08			67.30
141.00	1.07			67.70
142.00	1.06			68.10
143.00	1.05			68.50
144.00	1.04			68.90
145.00	1.03			69.30
146.00	1.02			69.70
147.00	1.01			70.10
148.00	1.00			70.50
149.00	0.99			70.90
150.00	0.98			71.30

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CHAPTER IV.
EXPERIMENTAL

PREPARATION OF PROPYLENE SULFIDE (METHYL THIIRANE):^{2,10}

One hundred sixteen grams (2 moles) of commercial propylene oxide was added slowly through a dropping funnel to 290 grams of water, and 292 grams (3 moles) of potassium thiocyanate in a one liter three-necked flask equipped with a mechanical blade stirrer and reflux condenser. The reaction mixture was kept cool with an ice-water bath during the addition. The rate of addition was controlled so as to require 40 to 50 minutes for the addition. The mixture was then stirred until the hour was completed. The temperature of the bath was then raised to 30 to 35°C. and stirred for another hour. The mixture was cooled and the crude propylene sulfide separated as a top layer. The crude propylene sulfide was washed twice with ice-water and then dried over CaCl_2 . Distillation gave some forerun, and the product was taken as the fraction boiling at 70-72°C., (usual barometric reading 680-685 mm. Hg.), n_D^{20} 1.4765. Average yield was 75% of theoretical. The forerun was collected and combined with foreruns from other preparations, and when a sufficient amount had been reserved, these were reacted again with potassium thiocyanate. Yields from the forerun material were

approximately 10% lower. Thiourea was used in place of the thiocyanate⁵ in the same molar proportions in some preparations, however, no improvement in yield could be noted.

OXIDATION OF PROPYLENE SULFIDE WITH 30% H₂O₂:

In a three-necked flask fitted with a reflux condenser, Herschberg stirrer, and dropping funnel, was placed 45.5 grams (0.4 moles) of 30% hydrogen peroxide ("Superoxol"). Before addition of the propylene sulfide was begun, the peroxide was brought to the addition temperature of the particular addition (Table I), since with some of the higher temperature additions the solution blew out through the reflux condenser if an excess of sulfide had been added while the peroxide was yet cold. When the peroxide was at the desired temperature, the addition of 7.4 grams (0.1 moles) of propylene sulfide through the dropping funnel was begun. This addition was slow, usually about 0.5 cc. per minute. The insertion of a thermometer into the reaction mixture for observation of the temperature was an aid in determining the rate of addition, as temperatures above 40°C. were liable to cause reactions violent enough to erupt through the reflux condenser. No explosion or decomposition sufficiently violent to rupture flasks was experienced. After the

addition was completed and the reaction mixture had been stirred at temperatures and intervals indicated in Table I, the excess peroxide was destroyed with "Catalase Sarett". The solution was then diluted to 100 ml. in a volumetric flask, and a 10 ml. portion taken for analysis. The 90 ml. of solution remaining were neutralized with excess Ba(OH)_2 in a round-bottomed flask fitted with a reflux condenser. This mixture was refluxed 18 hours. The precipitated barium sulfate was removed by centrifuging. Carbon dioxide was bubbled through the clear solution. The mixture was again centrifuged to free it from precipitated material. This process was repeated until no carbonate precipitate was evident. The solution was concentrated on the steam bath to about 10 to 20 ml.. The mixture was again filtered, as some BaCO_3 was precipitated from some bicarbonate which had been formed. Final concentration was accomplished under reduced pressure with a water aspirator. The barium hydroxypropane sulfonate was a syrupy sticky mass, but a greyish white powder when completely dry. Attempts at crystallization were made with this dried salt with 95% alcohol, but were unsuccessful. The dried material gave varying analyses for barium.

TREATMENT OF BARIUM HYDROXY PROPANE SULFONATE WITH PCl_5 :

In a round-bottomed flask fitted with reflux condenser was placed the dried barium salt (moles calculated as barium hydroxy propane sulfonate) with 25 ml. of chloroform and 4 molar equivalents of PCl_5 . This mixture was allowed to stand at room temperature until the evolution of hydrogen chloride had subsided, then it was placed on the steam cone and allowed to reflux for 12 hours. The reaction mixture was cooled to room temperature and then poured over cracked ice. The chloroform layer was separated. The water layer was extracted once with 15 ml. of chloroform. The two chloroform layers were combined and washed with 3 successive portions of cold water. The chloroform solution was dried over CaCl_2 overnight. After filtration through glass wool, the chloroform was removed on the aspirator. The oily product was distilled using the vacuum pump, with a boiling point of $54-55^\circ\text{C.}/1 \text{ mm.}$. The product could be distilled at a higher temperature and with less vacuum, but in the first distillations profound decompositions occurred if the pot temperature was in excess of 100°C. The redistilled product had a boiling point of $54-55^\circ\text{C.}/1 \text{ mm.}$, $77-78^\circ\text{C.}/8 \text{ mm.}$; n_D^{20} 1.4830.

PREPARATION OF THE METHYL ANILINE DERIVATIVE:

One and one-tenths grams of the chloropropane sulfonyl chloride from above (0.01 moles) in 10 cc. of ether was added with shaking to 3.3 grams (0.03 moles) of methyl aniline dissolved in 10 cc. of ether. The solution was allowed to stand for several hours. A precipitate of methyl aniline hydrochloride was formed, which was filtered off. The ether solution was washed two or three times with 1 N. HCl, and once with water. The ether was evaporated off and the residual oil was taken up in 95% alcohol. Water was added to the ethanol solution to the cloudy point. The mixture was placed in the refrigerator overnight. The precipitate was filtered off. The methyl anilide was recrystallized from ethanol and water, and had a melting point of 56-57.5°C. ¹³

Mixed melting point with the methyl anilide from the chlorosulfonyl chloride of sodium-2-hydroxypropane-1-sulfonate showed no depression.

CHLORINE WATER OXIDATION OF PROPYLENE SULFIDE:

In a 250 ml. flask fitted with reflux condenser, mechanical blade stirrer, dropping funnel, thermometer and gas inlet tube which led below the surface of the water, was placed 100 ml. of water. The flask was cooled with

an ice-water bath. Through the dropping funnel which had its end below the surface of the water to suppress direct chlorination, was added slowly 14.8 grams (0.2 moles) of propylene sulfide. Chlorine (tank) was passed in through the inlet tube. The ratio of the rate of addition of propylene sulfide and chlorine was such that an excess of chlorine was always present. Rate of addition of the propylene sulfide was regulated so that the reaction temperature did not rise above 10°C ., although rises to 15°C . for short periods of time did not impair the yield. After the propylene sulfide had been added, the rate of the chlorine addition was reduced and the mixture stirred for an additional hour. The addition of the chlorine was halted and air blown through the gas inlet tube to remove excess chlorine. The mixture was then separated and the heavy oily product washed three times with ice-water and dried over CaCl_2 overnight. The product was then distilled, at a boiling point of $55\text{-}56^{\circ}\text{C}/1\text{ mm.}$, $77\text{-}78^{\circ}\text{C}/8\text{ mm.}$; n_{D}^{20} 1.4859. Yields averaged 70% of theoretical.

Analysis Calcd. for $\text{C}_3\text{H}_5\text{SO}_2\text{Cl}_2$: C, 20.34; H, 3.41

Found: C, 20.54; H, 3.26.

The methyl aniline derivative was prepared in the manner described above, and had a melting point of $53.5\text{-}54.5^{\circ}\text{C}$.

Analysis Calcd. for $C_{10}H_{13}NO_2S$: N, 6.62; S, 14.75

Found: N, 6.84; S, 15.14

Mixed melting point with the methyl anilide from the chlorosulfonyl chloride of sodium-2-hydroxypropane-sulfonate showed a large depression, as the mixed melting point was below $50^{\circ}C$.

PREPARATION OF SODIUM 2-HYDROXYPROPANE-1-SULFONATE,
2-CHLOROPROPANE-1-SULFONYL CHLORIDE, AND METHYL
ANILINE DERIVATIVE:

Sixty-seven grams of propylene oxide (1.15 moles) was added with stirring to 95 grams of $Na_2S_2O_5$ in 200 ml. of water in a 500 ml. three-necked flask fitted with a reflux condenser, dropping funnel and mechanical blade stirrer. The reaction mixture was stirred at room temperature for 8 hours. The water was evaporated off, and the residue extracted with 90% ethanol. A white product was obtained which upon recrystallization from 95% ethanol gave a melting point of $225-227^{\circ}C$. The sodium 2-hydroxypropane-1-sulfonate was converted to the chloropropane sulfonyl chloride with PCl_5 . The 2-chloropropane-1-sulfonyl chloride had a boiling point of $51-52^{\circ}C./1\text{ mm.}$; n_D^{20} 1.4820. It was converted to the methyl aniline

derivative using the same procedure as for the methyl anilide from the peroxide oxidation. The methyl aniline derivative had a melting point of 57.2-58.2°C.

Analysis Calcd. for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20

Found: C, 56.85; H, 6.27

PREPARATION OF 2-CHLOROPROPANE-1-THIOL:

2-Chloropropane-1-thiol was prepared according to the methods of Davies and Savige.¹ In a 100 ml. round-bottomed flask fitted with a reflux condenser was placed 25 ml. (0.29 moles) of concentrated hydrochloric acid in 30 ml. of methanol. 14.8 grams (0.2 moles) of propylene sulfide in 20 ml. of methanol was added to the acid in small portions with cooling and shaking. The mixture was allowed to stand overnight. The mixture was then diluted with 100 ml. of water and the lower layer separated, and the aqueous layer extracted with 20 ml. of chloroform. The two portions were combined and dried over $CaCl_2$. Upon distillation a water-white product was obtained, with a boiling point of 60-62°C/82 mm.; n_D^{20} 1.4844. Yield was 50% of theoretical.

This product was oxidized with chlorine and water in the manner described for the oxidation of the propylene sulfide. The chloropropane sulfonyl chloride obtained had the following constants: Boiling point, 51°C./1 mm.; n_D^{20} 1.4827.

The methyl aniline derivative was prepared, giving a product with a melting point of 56.8-57.8°C.

A mixed melting point determination with the methyl aniline derivative from the chlorosulfonyl chloride of sodium 2-hydroxypropane-1-sulfonate showed no depression.

PREPARATION OF THE PHENYLHYDRAZINE DERIVATIVE OF THE HYDROXYPROPANE SULFONATE FROM THE PEROXIDE OXIDATION:¹²

The barium propane sulfonate was analyzed for barium by precipitation as barium sulfate. The free acid was then prepared by adding standard sulfuric acid to the analyzed sulfonate in a quantity slightly less than that required for complete precipitation of the barium. The free sulfonic acid was then reacted with an equimolar quantity of phenylhydrazine in alcohol. A granular precipitate was obtained. It was recrystallized from absolute ethanol. The recrystallized product had a melting point of 132-133°C.

Analysis Calcd. for $C_9H_{16}N_2O_4S$:

C, 43.53; N, 11.25; H, 6.5; S, 12.91.

Found: C, 43.25; N, 11.43; H, 6.05; S, 12.96 Ave.

This salt was titrated with standard base and the molecular weight determined:

Theoretical: M.W. 248.3

Found: M.W. 250.18

PREPARATION OF SODIUM PROPANE-2-OL-2-SULFONATE:

Eighty-seven grams (1.5 moles) of acetone was added with stirring to 142 grams (0.75 moles) of $\text{Na}_2\text{S}_2\text{O}_5$ in 275 ml. of water. The reaction mixture was kept below 20°C . by means of an ice-water bath. The time required for addition was 2 hours. Stirring was continued for $1\frac{1}{2}$ hours after the addition was completed. The solid product was filtered off.

ATTEMPTED PREPARATION OF PROP-1-ENE-2-SULFONYL CHLORIDE:

In a 50 ml. round-bottomed flask was placed 16.2 grams (0.1 mole) of acetone-bisulfite addition product, 12 ml. (0.15 moles) of thionyl chloride, and 20 ml. of chloroform. This mixture was allowed to reflux for 6 hours. An equivalent amount of KOH in ethyl alcohol was added with cooling and shaking. The KOH alcohol mixture was allowed to reflux overnight. The reaction mixture was neutralized with HCl and evaporated to dryness on the aspirator. The semi-dry mixture was treated with excess PCl_5 , and after it was refluxed for 12 hours, was poured over cracked ice and the water layer extracted with 100 cc. of chloroform. The chloroform solution was washed with 5 successive portions of cold water and then was dried over CaCl_2 . The chloroform was distilled off. The residual oil was distilled under reduced pressure. There was obtained as a product 2 grams of a colorless oil, which

darkened on standing. The boiling point was 66°C./12 mm.;
 n_D^{20} 1.3998. These constants are too low for the desired
compound. The methyl aniline derivative could not be
made from this compound.

Note: The carbon, hydrogen and nitrogen analyses cited
in this work were made by Clark Microanalytical Laboratory.
Sulfur analyses were made by the author.

CHAPTER V.

SUMMARY

a. The direct oxidation of propylene sulfide to the 2-hydroxypropane-1-sulfonic acid was accomplished with hydrogen peroxide. The direct oxidation of propylene sulfide to the 1-chloropropane-2-sulfonyl chloride was accomplished with chlorine water.

b. The structure of the oxidation products was proven by comparison with prepared chloropropane sulfonyl chlorides of known structure. The methyl aniline derivatives of these sulfonyl chlorides were prepared as solid derivatives for further comparison.

c. The hydroxypropane sulfonates which were prepared for comparison were made by methods yielding compounds of previously proven structure.

d. The cleavage of the sulfide ring of propylene sulfide may proceed either in a normal or an abnormal manner, the normal cleavage leading to products with the sulfur atom on the secondary carbon, the abnormal to products with the sulfur atom on the primary carbon. Peroxide oxidation was proven to proceed in an abnormal manner, while chlorine water oxidation gave the normal type of cleavage.

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