o-Benzamidophenol[16]: an amorphous, purple product, not reducible to *o*-benzamidophenol; did not react as expected with hydrogen chloride; apparently polymeric.

o-Benzenesulfonamidophenol[17]: tar.

o-Acetamidophenol (Eastman): tar.

6-Acetamido-*m*-cresol: at room temperature, the initial orange color of the solution lasted 2 minutes, then turned brown; at 0°, the orange color persisted, but the product decomposed when the solvent was removed.

6-Benzenesulfonamido-*m*-cresol: at room temperature, an immediate dark brown solution formed from which only amorphous, yellow, high-melting material was obtained; at 0°, the initially yellow solution began to turn brown in 3 minutes.

4-Chloro-6-benzamido-*m*-cresol: the orange solution obtained at room temperature appeared to be stable; the reaction was worked up after 5 minutes; the orange needles obtained were stable at room temperature for only about 10 minutes.

2-Benzenesulfonamido-*p*-cresol: an immediate dark brown solution formed which contained only brown, amorphous materials.

2-Benzamido-*p*-cresol[18]: at room temperature, the initial orange color lasted 15 seconds, then turned magenta; at −5°, the orange solution had become red in about 15 minutes; the purple product appeared to be polymeric.

2-Benzamido-4-chlorophenol: at room temperature, the orange color lasted for 10 minutes, then darkened; at 0°, the oxidation was slower, and after one hour only half of the amide had been oxidized; a few orange needles were isolated which were stable at room temperature for 5 minutes, and then decomposed to a yellow, amorphous solid.

3-Benzamido-4-hydroxybiphenyl[19]: at room temperature, the orange color was stable for 25 minutes; the reaction, when worked up after 5 minutes, gave orange needles, m.p. about 90°; the product was not sufficiently stable to recrystallize from ether.

2-Benzamido-4,6-dichlorophenol: at room temperature, an immediate orange color developed which appeared to be stable; a few orange crystals, m.p. 111–117°, were isolated which decomposed in about one hour at room temperature.

6-Benzamido-2,4-dimethylphenol[20]: at room temperature, the initially yellow solution darkened in a few minutes; at 0°, the yellow color appeared stable, but the product decomposed when the solvent was removed.

URBANA, ILLINOIS

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[16] J. H. Ransom, *Am. Chem. J.*, **23**, 17 (1900).

[17] C. B. Pollard and L. H. Amundsen, THIS JOURNAL, **57**, 357 (1935).

[18] K. v. Auwers and F. Eisenlohr, *Ann.*, **369**, 224 (1909).

[19] L. C. Raiford and J. C. Colbert, THIS JOURNAL, **47**, 1454 (1925).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MONTANA STATE UNIVERSITY]

Oxidative Ring Cleavage Reactions of Propylene Sulfide

BY JOHN M. STEWART AND HOWARD P. CORDTS

RECEIVED MARCH 28, 1952

Reactions of propylene sulfide with chlorine and bromine in various solvents, and with 30% hydrogen peroxide have been studied, and the mode of ring opening has been shown by proving the structure of the products formed. Addition of chlorine and bromine to propylene sulfide in anhydrous solvents caused ring cleavage at the primary carbon–sulfur bond to give bis-(1-methyl-2-haloethyl) disulfides. Reversing the manner of addition and adding the propylene sulfide to liquid chlorine or bromine gave 1-halo-2-propanesulfenyl halides plus more highly halogenated compounds. Aqueous chlorine also cleaved the sulfide ring at the primary carbon to give 1-chloro-2-propanesulfonyl chloride. In the reactions of 30% hydrogen peroxide with propylene sulfide small yields of 2-hydroxy-1-propanesulfonic acid, formed by ring cleavage at the secondary carbon–sulfur bond, were obtained, and sulfuric acid was also identified as a chief product in these reactions. Derivatives of these compounds were prepared and compared to compounds made by unequivocal methods.

Introduction

In the few studies which have been made on the structure of the addition products of unsymmetrical olefin sulfides, it has been found that amines open the isobutylene sulfide ring mainly at the primary carbon[1]; mercaptans with isobutylene sulfide and either acidic (boron trifluoride) or basic (sodium ethoxide) catalysis give mixtures of products resulting from opening of the ring at either the tertiary or primary carbon[2]; alcohols with isobutylene sulfide and acidic (boron trifluoride) catalysis give mainly ring opening at the tertiary carbon[2]; hydrochloric acid in methanol, and acid chlorides with either propylene sulfide or chloropropylene sulfide open the rings mainly at the secondary carbon.[3,4]

Most of the previously published investigations of the reactions of olefin sulfides have led to products which were mercaptans or esters of mercaptans. In this work propylene sulfide has been treated with oxidizing types of reagents to yield products other than mercaptans, and the direction of cleavage of the sulfide ring has been shown by proof of the structure of these products.

Discussion

Addition of either chlorine or bromine to propylene sulfide in an anhydrous solvent such as chloroform gave excellent yields of bis-(halopropyl) disulfides. The structure, as shown in the accompanying diagram of reactions (Fig. 1), is for the isomer proved to be the main product—the cleavage of the sulfide ring proceeding at the primary carbon to give bis-(1-methyl-2-chloroethyl) disulfide (I) or the corresponding bromine compound. Using a solution of bromine in carbon tetrachloride of known concentration, a solution of propylene sulfide in the same solvent could be titrated to a color end-point, and the reaction was found to be quantitative.

Compound I, or its bromine analog, on treatment with excess piperidine gave bis-(1-methyl-2-piperidinoethyl) disulfide, isolated as the dihydrochloride salt. The amine was desulfurized with Raney nickel and the only new amine isolated from the reaction was proved through the melting point of

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[1] H. R. Snyder, J. M. Stewart and J. B. Ziegler, THIS JOURNAL, **69**, 2672 (1947).

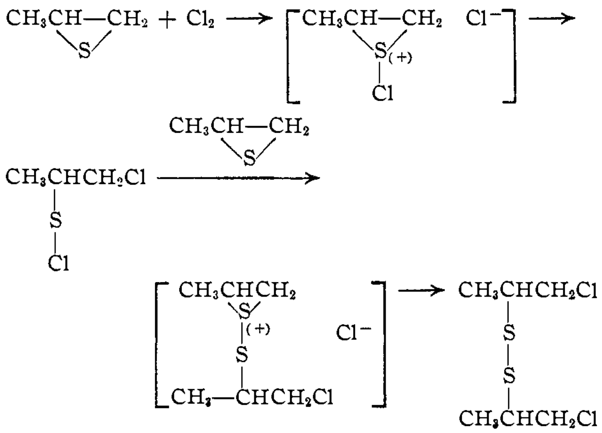
[2] H. R. Snyder, J. M. Stewart and J. B. Ziegler, *ibid.*, **69**, 2675 (1947).

[3] W. Davies and W. E. Savige, *J. Chem. Soc.*, 317 (1950).

[4] W. Davies and W. E. Savige, *ibid.*, 774 (1951).

its picrate salt to be N-*n*-propylpiperidine and not N-isopropylpiperidine. This was not regarded as rigid proof of structure by itself, since the possibility of rearrangement during the reaction with piperidine had not been excluded. However, in view of the further proof of structure given below, it appears that no such rearrangement does occur.

It is possible that the reaction occurring when halogens are added to propylene sulfide under anhydrous conditions may proceed in two steps—the first an addition of one molecule of halogen to one of sulfide to form a 1-halo-2-propanesulfenyl halide, followed by a rapid reaction of this compound with another molecule of propylene sulfide to give the bis-(1-methyl-2-haloethyl) disulfide. The following mechanism is proposed



That this may be the case was demonstrated by some experiments in which the manner of addition of reactants was reversed, and propylene sulfide was added dropwise to a molar equivalent of liquid chlorine or bromine. The 1-halo-2-propanesulfenyl halides were obtained, although mixed with sulfenyl halides containing larger amounts of halogen from which separation was difficult. In one case 1-chloro-2-propanesulfenyl chloride (II) was obtained in a fairly pure state and on reaction with propylene sulfide gave I.

Compound I was converted by treatment with chlorine in 80% acetic acid to 1-chloro-2-propanesulfonyl chloride (III). On reaction of III with excess N-methylaniline a solid derivative, m.p. 54–55°, N-methyl-1-propene-2-sulfonanilide (IV) was obtained. Schroeter and Salzbacher[5] prepared a compound which they claimed to have structure IV but which they reported to have a melting point of 58–59°. This melting point is in agreement with that of the isomer, N-methyl-1-propene-1-sulfonanilide (V) prepared by the authors by unequivocal methods and also reported by Autenrieth.[6] When IV was mixed with V a large depression of melting point was observed, thus affording further proof of the structure of the halogen–propylene sulfide addition products. There was no indication at any time that any appreciable amounts of the isomers were formed in which the sulfur atom remains attached at the primary carbon.

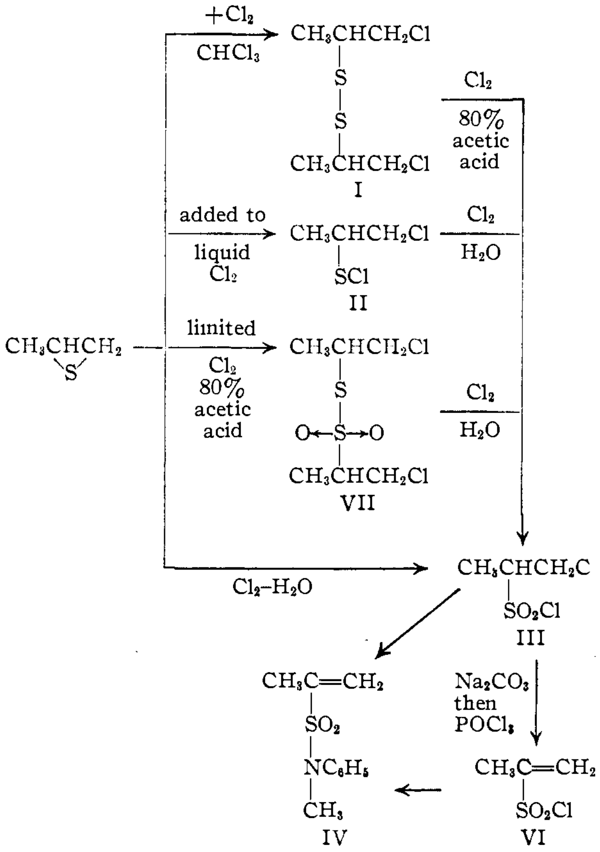
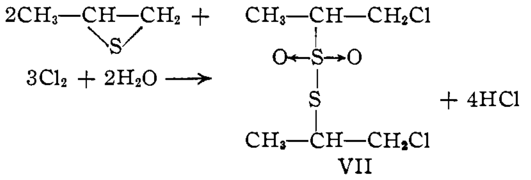


Fig. 1.

Compound III was also converted to IV by an indirect route—first by dehydrohalogenation with sodium carbonate converting it to sodium 1-propene-2-sulfonate and then treatment with phosphorus oxychloride yielding 1-propene-2-sulfonyl chloride (VI). Compound VI with N-methylaniline then gave IV.

When propylene sulfide was oxidized directly with chlorine water, cleavage again proceeded at the primary carbon–sulfur bond—a good yield of only one of the possible isomers, 1-chloro-2 propanesulfonyl chloride (III), being obtained. This product had the same boiling point and refractive index as the compound obtained by chlorine water oxidation of I, and on treatment with N-methylaniline gave a derivative identical with IV.

In one experiment in which propylene sulfide was dissolved in 80% acetic acid and treated with chlorine to a point at which an excess of chlorine first became apparent, the principal product was found to be an oxidation product intermediate between I and III which had the correct analysis for VII. This experiment was then repeated but using the calculated amount of chlorine in accordance with the equation



VII

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(5) G. Schroeter and M. Salzbacher, *Ber.*, **61B**, 1616 (1928).

(6) W. Autenrieth, *ibid.*, **34**, 3467 (1901).

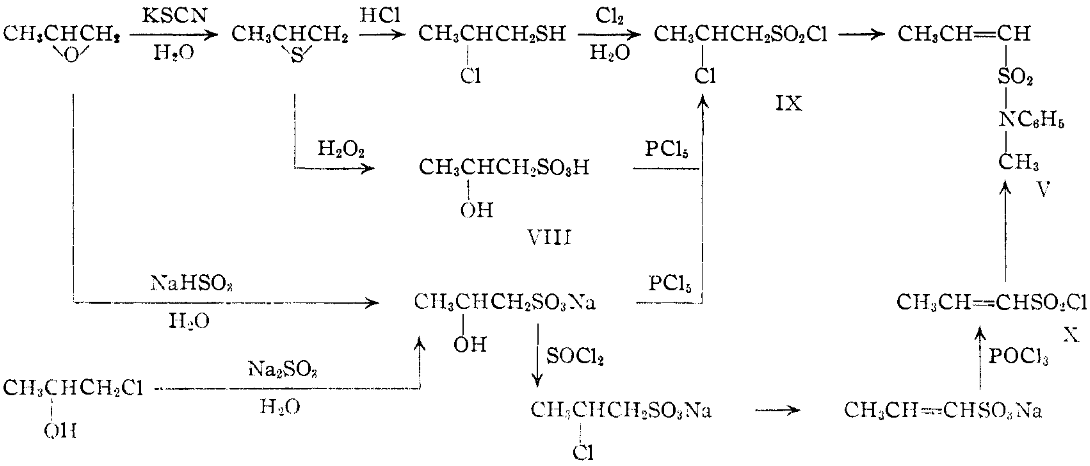

Fig. 2.

and VII was obtained in 50% yield together with some I and some III.

Use of 30% hydrogen peroxide as oxidizing agent led to two identified sulfur-containing acids. About 33% of the sulfide was converted into sulfuric acid by complete cleavage and oxidation of the sulfur atom. The other sulfur-containing acid proved to be a product formed by cleavage of the ring at the secondary carbon–sulfur bond, 2-hydroxy-1-propanesulfonic acid (VIII), isolated as the barium salt and identified by analysis of the phenylhydrazine salt. The over-all yield of purified barium salt obtained was small, amounting to between 14 and 25% based on propylene sulfide. There was, however, no indication in any of the experiments that the isomeric sulfonic acid was formed in any appreciable amount. In order to prove the structure of VIII, its barium salt was converted by treatment with phosphorus pentachloride into 2-chloro-1-propanesulfonyl chloride (IX). This compound differed from III in refractive index and gave an N-methylaniline derivative (V) of the same analysis as IV but differing in melting point. A mixture of IV with V had a melting point much lower than either alone. The compound V then must be N-methyl-1-propene-1-sulfonanilide. As further proof, a mixed melting point of V with N-methyl-1-propene-1-sulfonanilide made in an unequivocal manner showed no depression.

In order to prove conclusively the structure of the propylene sulfide oxidation products in which the cleavage products were of the type with the sulfur remaining on the primary carbon, these compounds were also prepared by the following two unequivocal methods, as diagrammed in Fig. 2: (1) Treatment of 1-chloro-2-propanol with sodium sulfite gave sodium 2-hydroxy-1-propanesulfonate. The same compound was also made by reaction of propylene oxide and sodium bisulfite. This salt was converted by phosphorus pentachloride to 2-chloro-1-propanesulfonyl chloride (IX). Compound IX was then treated with N-methylaniline to obtain N-methyl-1-propene-1-sulfonanilide (V). By an alternate route, sodium 2-hydroxy-1-propanesulfonate could be first converted to sodium 2-chloro-1-propanesulfonate, this dehydrohalogenated to give sodium 1-propene-1-sulfonate and this treated with phosphorus oxychloride to give 1-propene-1-sulfonyl chloride (X). Compound X with N-methylaniline then yielded V. (2) Davies and Savige[4] have proved through a series of reactions that addition of hydrochloric acid to propylene sulfide proceeds with cleavage at the secondary carbon–sulfur bond to yield 2-chloro-1-propanethiol. This compound was made according to their directions and was then oxidized by chlorine water to 2-chloro-1-propanesulfonyl chloride (IX). The N-methylaniline derivative (V) was again prepared from this compound.

It would appear that the mechanism of the ring-opening reactions of olefin sulfides might follow one of the possible courses postulated for the ring openings of the analogous olefin oxides.[7,8] The nature of the attacking reagent and of any catalyst used, and the presence of substituent groups in the olefin sulfide molecule should all play a part in determining the reaction mechanism followed, and also the point of cleavage in unsymmetrical olefin sulfides.

Acknowledgment.—The authors acknowledge gratefully a F. G. Cottrell Grant from the Research Corporation in support of this work.

Experimental[9]

Propylene Sulfide.—Propylene sulfide was prepared as described by Snyder, Stewart and Ziegler[1] by stirring a mixture of propylene oxide and aqueous potassium thiocyanate solution. Yields averaged 65%.

Bis-(1-methyl-2-bromoethyl) Disulfide.—A solution of known concentration of bromine in carbon tetrachloride was added dropwise with stirring to a chilled solution of 8.535 g. of propylene sulfide in 25 ml. of carbon tetrachloride until a persistent yellow color appeared. The 0.115 mole of sulfide absorbed 9.1 g. (0.114 gram atom) of bromine. The solution was washed twice with 5% sodium carbonate solution and dried over calcium chloride. Distillation gave 15.6 g. (88%) of colorless liquid, b.p. range 114-117° (1 mm.), n^{20}_{D} 1.5838.

Anal. Calcd. for $C_6H_{12}Br_2S_2$: C, 23.29; H, 3.92; Br, 51.88. Found[10]: C, 23.28; H, 3.64; Br, 51.92.

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[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 302-303.

[8] R. G. Kadesch, THIS JOURNAL, **68**, 43 (1946).

[9] All melting points are uncorrected.

[10] Microanalyses for carbon, hydrogen, nitrogen and halogen reported in this work were carried out by the Clark Microanalytical Laboratory, Urbana, Ill. Sulfur analyses were done by the authors.

Bis-(1-methyl-2-chloroethyl) Disulfide (I).—Liquid chlorine, 8 g. (0.226 gram atom), was collected in a Dry Ice-cooled tube and then allowed to vaporize into an ice-cooled and stirred solution of 16.7 g. (0.226 mole) of propylene sulfide in 120 ml. of chloroform. The color changed to a permanent light yellow near the end of the addition. On removal of the chloroform under vacuum, some of the product was lost by foaming over of the solution. The crude product weighed 19.5 g. On distillation there was obtained 17.5 g. (71%) of a colorless oil, b.p. range 98–101° (1 mm.), n^{20}D 1.5400. The derivative described below was prepared for analysis.

Bis-(1-methyl-2-piperidinoethyl) Disulfide.—Either the chlorine- or bromine-propylene sulfide addition product from above was heated with excess piperidine in alcohol and the crude product was purified as the dihydrochloride salt of bis-(1-methyl-2-piperidinoethyl) disulfide, m.p. 225–226° after recrystallization from alcohol-ether.

Anal. Calcd. for $C_{16}H_{34}Cl_2N_2S_2$: S, 16.46. Found: S, 16.40, 16.38.

A solution of crude bis-(1-methyl-2-piperidinoethyl) disulfide in ethanol was desulfurized with Raney nickel. The amine product was obtained in only 25% yield of theory and was converted to its picrate salt, m.p. 107–108° on recrystallization from absolute ethanol. N-*n*-Propylpiperidine picrate is reported by Magnusson and Schierz[11] to have a melting point of 108°, whereas N-isopropylpiperidine picrate has a melting point of 153°.

Addition of Propylene Sulfide to Chlorine. 1-Chloro-2-propanesulfenyl Chloride (II).—Liquid chlorine, 5.0 g. (0.07 mole), and 10 ml. of chloroform were mixed and cooled in a Dry Ice-acetone-bath while 5.7 g. of propylene sulfide (0.077 mole) in 40 ml. of chloroform (precooled in a Dry Ice-bath) was added over a period of 10 minutes. Argon was then bubbled through the mixture to remove any unreacted chlorine and the solvent was stripped at room temperature. On distillation of the crude product it was apparent from the lack of definite boiling point that a mixture was present. However, 3.6 ml. of orange liquid boiling from 40–50° (4.5 mm.) was redistilled to yield 2 g. (20%) of orange liquid, b.p. 44–47° (6 mm.), n^{19}D 1.5200. The higher boiling liquid products were apparently more highly chlorinated.

The product was not directly analyzed but was treated at once with propylene sulfide and thus converted to the previously prepared bis-(1-methyl-2-chloroethyl) disulfide. The reaction was rapid and the solution of product was colorless. Distillation yielded a colorless oil, b.p. 96–98° (1 mm.), n^{19}D 1.5420. These constants compare closely to those of bis-(1-methyl-2-chloroethyl) disulfide (I) obtained by addition of chlorine to propylene sulfide.

Addition of Propylene Sulfide to Bromine.—To a chilled solution of 8.37 g. (0.052 mole) of bromine in 45 ml. of chloroform was added 4 g. (0.054 mole) of propylene sulfide in 25 ml. of chloroform. The addition required 30 minutes. When the solvent had been stripped, leaving a red-colored oil, attempted distillation under vacuum resulted in decomposition. In an identical experiment the crude chloroform solution of 1-bromo-2-propanesulfenyl bromide was added dropwise directly to a solution of 4 g. of propylene sulfide in 25 ml. of chloroform. The deep red color disappeared during this addition. Distillation of the product gave 1 ml. of combined forerun and afterrun and 7.6 g. of slightly yellow oil, b.p. 109–112° (1 mm.), n^{19}D 1.5848. These constants agree closely with those of bis-(1-methyl-2-bromoethyl) disulfide obtained by direct addition of bromine to propylene sulfide, and reaction with piperidine gave the same derivative, isolated as the dihydrochloride, m.p. 226–227°.

Aqueous Chlorine Oxidation of Bis-(1-methyl-2-chloroethyl) Disulfide.—Attempts to oxidize the bis-(1-methyl-2-chloroethyl) disulfide by chlorine in a water suspension failed. It was successfully done in 80% acetic acid. External cooling was used to keep the reaction temperature below 40°. From 2.2 g. of disulfide there was obtained 2.4 g. (68%) of colorless liquid product, b.p. 49–51.5° (1 mm.), n^{20}D 1.4860. These constants are the same as those for the product of direct aqueous chlorine oxidation of propylene sulfide, 1-chloro-2-propanesulfonyl chloride (III) (for analysis see below). The melting point of the N-methylaniline derivative (IV) of this product was 53.5–55°.

1-Chloro-2-propanesulfonyl Chloride (III). Aqueous Chlorine Oxidation of Propylene Sulfide.—To 100 ml. of saturated chlorine water was added dropwise with stirring 14.8 g. (0.2 mole) of propylene sulfide, the dropping funnel having its end below the water solution. Concurrently chlorine was bubbled through the mixture at such a rate that an excess was always present. The reaction temperature was maintained at 0–12° by means of an ice-bath and control of the rate of propylene sulfide addition. After the propylene sulfide had been added, the rate of chlorine addition was reduced and stirring was continued for an hour. Air was then bubbled through the mixture to remove excess chlorine. The heavy oily product was separated, washed three times with ice-water and dried over calcium chloride. On distillation, the colorless liquid product boiled at 55–56° (1 mm.) or 77–78° (8 mm.), n^{20}D 1.4859. Yields averaged 24.8 g. (70%).

Anal. Calcd. for $C_3H_6SO_2Cl_2$: C, 20.34; H, 3.41. Found: C, 20.54; H, 3.26.

The N-methylaniline derivative (IV) prepared as described below had a melting point of 54–55°. Approximately two equivalents of N-methylaniline hydrochloride were formed as by-product from this reaction.

Anal. Calcd. for $C_{10}H_{13}NO_2S$: N, 6.62; S, 15.15. Found: N, 6.84; S, 14.75, 15.50.

1-Propene-2-sulfonyl Chloride (VI).—From 8 g. of 1-chloro-2-propanesulfonyl chloride, which was treated first with concentrated aqueous sodium carbonate to form sodium 1-propene-2-sulfonate and then with excess phosphorus oxychloride, there was obtained on final distillation 2 g. (31.5%) of colorless liquid, b.p. 70–75° (10 mm.), n^{20}D 1.4740. This material was not analyzed directly but gave N-methyl-1-propene-2-sulfonanilide (IV) and only one equivalent of N-methylaniline hydrochloride on treatment with N-methylaniline.

Preparation of Methylaniline Derivatives of the Chloropropanesulfonyl Chlorides.—To a solution of 3.5 g. (0.033 mole) of N-methylaniline in 25 ml. of ether was added 1.77 g. (0.01 mole) of the chloropropanesulfonyl chloride. In the case of the primary sulfonyl chloride an immediate reaction ensued, while with the secondary sulfonyl chloride there was a short induction period. The mixture was allowed to stand for 18 hr. at room temperature and the precipitated methylaniline hydrochloride was filtered off. The ether solution was washed twice with 5% hydrochloric acid and once with water and dried over calcium chloride. The ether was evaporated off. Purification was accomplished by several recrystallizations from methanol-water mixtures.

Oxidation of Propylene Sulfide in 80% Acetic Acid with Controlled Amount of Chlorine. Preparation of (VII).—A slight excess over the calculated amount of liquid chlorine (14.6 g. or 0.206 mole) was collected in a Dry Ice-cooled trap and this amount was then allowed to evaporate slowly and passed into an ice-cooled and rapidly stirred mixture of 10 g. of propylene sulfide (0.135 mole), 50 ml. of acetic acid and 12 ml. of water. This mixture was clear at the start, became milky as the chlorine was passed in and then became clear and homogeneous again just before all the chlorine had been added. After the addition of chlorine was completed, the ice-bath was removed and stirring continued for 15 minutes at room temperature. The product was then isolated as described for other chlorination products. On first distillation there was obtained a forerun between 58 and 126°, and 8.5 g. (50%) of slightly tan liquid boiling between 127° and 137° (1 mm.), n^{20}D 1.5283. On redistillation the material was divided arbitrarily into three fractions boiling between 144 and 150° at 1 mm., but all had the same refractive index, n^{20}D 1.5285.

Anal. Calcd. for $C_6H_{12}Cl_2O_2S_2$: C, 28.69; H, 4.82. Found: C, 28.65; H, 4.62.

This intermediate oxidation product was then further treated with excess chlorine in water and converted to 1-chloro-2-propanesulfonyl chloride, n^{20}D 1.4858.

Hydrogen Peroxide Oxidation of Propylene Sulfide.—In a typical experiment 7.4 g. (0.1 mole) of propylene sulfide was added dropwise over a period of 30–45 minutes to 46 g. of 30% hydrogen peroxide with rapid stirring. The temperature was held below 40° by external cooling and control of the rate of propylene sulfide addition. After the addition was completed, the mixture was stirred for an additional hour at temperatures which were varied from 20 to 80°—the tem-

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(11) H. W. Magnusson and E. R. Schierz, Univ. of Wyoming Pub. 7, 1-11 (1940).

perature apparently having no effect on the products obtained. Excess peroxide was then destroyed with "Catalase Sarrett," the solution was diluted to 100 ml. in a volumetric flask and a 10-ml. aliquot was taken for titration studies. Titration and analysis showed an average ratio of one part of sulfuric acid to three parts of total acid. The remaining 90 ml. of solution was neutralized by refluxing with excess barium hydroxide. Precipitated barium sulfate was removed by centrifuging. Carbon dioxide was then bubbled through the solution and the mixture was again centrifuged. This process was repeated until no more barium carbonate precipitate was evident. The solution was concentrated to 15 ml. and again filtered. Final concentration was accomplished at reduced pressure, leaving the barium sulfonate as a sirupy mass. On removal of remaining water in a vacuum desiccator, the salt was obtained as a gray-white powder, in yields ranging from 3.0 g. (14.5%) to 5.0 g. (24%). Analyses for barium indicated that small amounts of inorganic salts were still present. The impure barium 2-hydroxypropanesulfonate was converted to the free sulfonic acid with the calculated amount of sulfuric acid. Treatment with phenylhydrazine in alcohol gave a granular precipitate which on recrystallization from alcohol melted at 132–133°.

Anal. Calcd. for $C_9H_{16}N_2O_4S$: C, 43.53; H, 6.5; N, 11.25; S, 12.91; mol. wt., 248.3. Found: C, 43.25; H, 6.05; N, 11.43; S, 12.96; mol. wt., 250.2.

Part of the barium hydroxypropanesulfonate was converted to a chloropropanesulfonyl chloride with phosphorus pentachloride. The product had a boiling point of 54–55° (1 mm.), $n^{20}\mathrm{D}$ 1.4830. The N-methylaniline derivative of this material had a melting point of 57.5–58.5°, corresponding to that of N-methyl-1-propene-1-sulfonanilide (V) as prepared by Autenrieth.[7]

Sodium 2-Hydroxypropane-1-sulfonate (a).—A mixture of 19 g. (0.2 mole) of 1-chloro-2-propanol and 31.5 g. (0.25 mole) of sodium sulfite in 75 ml. of water was heated in a steel hydrogenation-type bomb for 8 hr. at 180°. The reaction mixture was filtered and the solution was evaporated to dryness. Three extractions with 90% ethanol followed by evaporation of the ethanol gave 30 g. of somewhat waxy white solid. This on drying in a vacuum desiccator yielded finally 25 g. (77.2%) of crystalline salt. **(b) Propylene oxide–Sodium Bisulfite Addition Reaction.**—A mixture of 95 g. (0.5 mole) of sodium metabisulfite and 67 g. (1.16 mole) of propylene oxide in 200 ml. of water was stirred at room temperature for 8 hr. and the solution was then evaporated to dryness. The crude product was recrystallized from 90% ethanol and a total of 138 g. (85.2%) of sodium 2-hydroxy-1-propanesulfonate was obtained. A small portion after a second recrystallization from 95% ethanol had a melting point range of 225–227°.

2-Chloro-1-propanesulfonyl Chloride (IX).—This compound was obtained from sodium 2-hydroxy-1-propanesulfonate by treatment with excess phosphorus pentachloride. Yields ranged from 25 to 50% of (IX), b.p. 62–65° (2.5 mm.), $n^{20}\mathrm{D}$ 1.4818.

Treatment with N-methylaniline gave N-methyl-1-propene-1-sulfonanilide (V), m.p. 58–59°.

Anal. Calcd. for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20. Found: C, 56.85; H, 6.27.

1-Propene-1-sulfonyl Chloride (X).—A mixture of 32.4 g. (0.2 mole) of sodium 2-hydroxy-1-propanesulfonate and 35 ml. of thionyl chloride was allowed to react at room temperature for two hours and then warmed at 50–70° for a further two hours. It was then poured into water, an excess of sodium carbonate was added and the mixture was evaporated to dryness. Extraction with hot 95% ethanol and removal of ethanol from the extracts left 20 g. of white salt, sodium 1-propene-1-sulfonate. The salt was heated at the steam-cone with 38 g. of phosphorus oxychloride for an hour and the product was worked up as described for other sulfonyl chlorides. On distillation there was obtained some forerun, a main fraction of 8 g. (28%), b.p. 67.5–69° (8 mm.), $n^{20}\mathrm{D}$ 1.4756, and some much higher boiling material. Part of the main fraction was converted to the N-methylaniline derivative, m.p. 57–58°, which showed no depression of melting point when mixed with the N-methylaniline derivative made from 2-chloro-1-propanesulfonyl chloride.

2-Chloro-1-propanethiol.—This compound was prepared according to the directions of Davies and Savige[4] by the reaction of propylene sulfide and hydrochloric acid in methanol solution. The compound had a boiling point of 60–62° (82 mm.), $n^{20}\mathrm{D}$ 1.4844.

Chlorine Water Oxidation of 2-Chloro-1-propanethiol.—The procedure used was the same as that described for the chlorine water oxidation of propylene sulfide. The product, 2-chloro-1-propanesulfonyl chloride, b.p. 51° (1 mm.), gave N-methyl-1-propene-1-sulfonanilide, m.p. 57–59°, on reaction with N-methylaniline.

MISSOULA, MONTANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XXV. Cycloöctanediols. Molecular Rearrangement of Cycloöctene Oxide on Solvolysis[1]

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Hydroxylation of *cis*-cycloöctene with performic acid, and hydrolysis or solvolysis with formic acid of *cis*-cycloöctene oxide, have been found to yield 1,4-cycloöctanediol in larger amount than the expected product, *trans*-1,2-cycloöctanediol. The structure of 1,4-cycloöctanediol was established by conversion to cycloöctane through the diacetate and cycloöctadiene, and by Oppenauer oxidation to 1,4-cycloöctanedione, which by an intramolecular aldol condensation formed the known ketone, bicyclo[3.3.0]-1(5)-octen-2-one. The molecular rearrangement resulting in formation of the 1,4-glycol is interpreted as a chemical "transannular effect" which permits participation in the solvolysis of the epoxide by a carbon–hydrogen bond that is sterically adjacent because of its location across the compact eight-membered ring. *cis*-1,2-Cycloöctanediol and the eight-membered cyclic acyloin suberoin have been prepared and characterized.

Before cycloöctene from the partial hydrogenation of cycloöctatetraene[4] was available as an intermediate for the synthesis of other eight-membered ring compounds such as 1,3-cycloöctadiene,[5] an investigation of the preparation of 1,2-cycloöctanediols (and 1,3-cycloöctadiene) from the cyclic acyloin suberoin was undertaken. When cyclooctene became available, it was converted into *cis*- and *trans*-1,2-cycloöctanediols. This phase of the work led to discovery of an unusual rearrangement that occurs during the solvolysis of cyclooctene oxide.

The acyloin condensation of dimethyl suberate, under conditions similar to those used for the

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[3] Abstracted in part from the Ph.D. dissertation of Claude F. Spencer, Massachusetts Institute of Technology, June, 1950.

[4] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[5] A. C. Cope and L. L. Estes, Jr., THIS JOURNAL, **72**, 1128 (1950).