layer, was dried and distilled to give 16 g. (14%) of benzyl alcohol, b.p. 92° (9 mm.), $n^{20}\mathrm{D}$ 1.5388, 11 g. of biphenyl, b.p. 75–85° (1 mm.) and 43 g. (33%) of a viscous oil, b.p. 158–163° (1 mm.), $n^{20}\mathrm{D}$ 1.5990, and a large resinous residue.

The aqueous layer was acidified with 6 *N* hydrochloric acid to yield, after recrystallization from water, 14 g. (12%) of benzoic acid, m.p. 121°.

The propylene was identified as the dibromo compound, 40 g. (20%), b.p. 141°, m.p. −55°, $n^{20}\mathrm{D}$ 1.5199 (lit.[13] b.p. 141°, m.p. −55.6°, $n^{20}\mathrm{D}$ 1.5203). The α-naphthylurethan, m.p. 133–134° (lit.[14] m.p. 134.5°) and 3,5-dinitrobenzoate, m.p. 112–113° (lit.[15] m.p. 112°) of benzyl alcohol were not depressed on admixture with authentic material. The biphenyl, m.p. 69°, did not depress the melting point of authentic biphenyl. The *p*-bromophenacyl ester, m.p. 117–118° (lit.[16] 119°) and the amide, m.p. 129° (lit.[17] m.p. 130°) of benzoic acid were not depressed by the derivatives of authentic material.

The viscous oil was found to readily decolorize bromine solutions and on oxidation with potassium permanganate in acetone[18] gave benzoic acid. A molecular weight of 263 by the Rast method indicated that the compound was probably the dimer of phenylbutadiene, molecular weight 260 (lit.[8] b.p. 160° (1 mm.), $n^{20}\mathrm{D}$ 1.5988).

Permanganate oxidation of 15 g. of the resinous residue gave 5 g. of benzoic acid.

Preliminary attempts to prepare the oxides by treatment of the chlorohydrins or the acetates thereof with a molten mixture of potassium and sodium hydroxides[19] gave large quantities of gaseous olefin and, in the case of IV, no product was obtained in the anticipated boiling range of the oxide.

β-Chloropropionaldehyde was prepared by the passage of three moles of hydrogen chloride into an ethereal solution of three moles of acrolein while maintaining the temperature below −10°. The ethereal solution was shaken with anhydrous potassium carbonate and calcium chloride and utilized in the Grignard reaction without further purification.

4-Chloro-2-butanol.—The reaction of β-chloropropionaldehyde and the Grignard reagent prepared from 72.9 g. (3 moles) of magnesium and 426 g. (3 moles) of methyl iodide gave a 33% yield of 4-chloro-2-butanol, b.p. 48–50° (2 mm.). In order to obtain pure product the bath temperature was maintained below 80° during the distillation.

4-Chloro-2-acetoxybutane.—A mixture of 132 g. (1.2 moles) of 4-chloro-2-butanol and 150 ml. (1.45 moles) of acetic anhydride in the presence of a few drops of concentrated sulfuric acid was shaken intermittently for 30 minutes while an exothermic reaction took place. The reaction mixture was then refluxed for 1.5 hours and decomposed with water. The organic layer was separated, washed with water and dried over anhydrous sodium carbonate. The crude product obtained by atmospheric distillation was redistilled *in vacuo* to yield 149 g. (83%) of ester, b.p. 68–70° (11 mm.).

1-Methyltrimethylene Oxide.—A mixture of 196 g. (4.9 moles) of sodium hydroxide, 196 g. (3.5 moles) of potassium hydroxide and 15 ml. of water was heated in a 1-l. flask equipped with a dropping funnel, thermometer, stirrer and a 15-in. Vigreux column connected to a water-cooled condenser with an ice-cooled receiver. The temperature was raised to 160° and 200 g. (1.33 moles) of 4-chloro-2-acetoxybutane was rapidly added dropwise with efficient stirring over a period of 45 minutes. The temperature was maintained between 150–160° during the addition while the vigorous reaction produced white fumes which were collected in the cooled receiver. The vapor temperature of the distillate was 60–70°. Distillation ceased on the completion of the addition and the reaction temperature was slowly raised to 220° over a period of one hour while additional distillate was collected. The crude distillate, 83 g., was fractionated through a 1.5-ft. helices-packed column to yield 65 g. (68%) of oxide, b.p. 59–60°, $n^{25}\mathrm{D}$ 1.3886 (lit.[3b] b.p. 59.4–59.7° (736 mm.), $n^{20}\mathrm{D}$ 1.3889).

Infrared absorption spectra of the trimethylene oxides were obtained in a 0.025-mm. cell with a Perkin–Elmer spectrophotometer.

Acknowledgments.—We wish to acknowledge the assistance of Robert C. Petry and Paul F. Forsyth who prepared 1-methyltrimethylene oxide and its precursors.

BUFFALO, NEW YORK

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(14) V. T. Bickel and H. E. French, THIS JOURNAL, **48**, 747 (1926).

(15) O. Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., p. 166.

(16) W. L. Judefind and E. E. Reid, THIS JOURNAL, **42**, 1043 (1920).

(17) Reference 12a, p. 363.

(18) C. N. Riiber, *Ber.*, **37**, 2275 (1904).

(19) S. Searles, THIS JOURNAL, **73**, 124 (1951).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

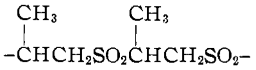
The Structure of Propylene Polysulfone

BY C. S. MARVEL AND E. D. WEIL[1]

RECEIVED JUNE 24, 1953

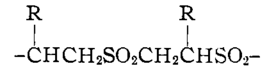
Evidence originally presented in support of the postulated "head-to-head" structure of olefin–sulfur dioxide copolymers has been re-examined and found to have been misleading because of certain previously-unrecognized rearrangements which occurred during the synthesis of reference compounds. Evidence has been found for a "head-to-tail" structure in the propylene–sulfur dioxide copolymer. The oxidation product of polymerized propylene sulfide has been found to be similar in structure to the propylene–sulfur dioxide copolymer.

The earliest publications describing the copolymer of propylene and sulfur dioxide presented conflicting opinions on the structure of this polymer. Staudinger and Ritzenthaler[2] proposed a "head-to-tail" structure I but presented no experimental evidence for this proposal. Marvel and co-workers[3-6] investigated the structure of the copolymers of sulfur dioxide with propylene, pentene-1, styrene, and 10-hendecenoic acid, and proposed a "head-to-head, tail-to-tail" structure (II) for these substances on the basis of degradation reactions and syntheses of the degradation products by reactions believed at that time to be unequivocal.



$$-\overset{\overset{\textstyle CH_3}{|}}{C}HCH_2SO_2\overset{\overset{\textstyle CH_3}{|}}{C}HCH_2SO_2-$$

I



$$-\overset{\overset{\textstyle R}{|}}{C}HCH_2SO_2CH_2\overset{\overset{\textstyle R}{|}}{C}HSO_2-$$

II, R = CH_3-, $CH_3CH_2CH_2-$, C_6H_5- or $HO_2C(CH_2)_8-$

Subsequent to these investigations, an increasingly large body of evidence has accumulated showing that in polymers formed by the free-radical mechanism the monomer units comprising the polymer chain are arranged predominantly in the head-to-tail manner; no vinyl homopolymer is now

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(1) National Science Foundation Fellow 1952–1953.

(2) H. Staudinger and B. Ritzenthaler, *Ber.*, **68**, 455 (1935).

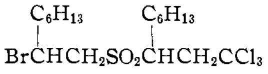
(3) M. Hunt and C. S. Marvel, THIS JOURNAL, **57**, 1691 (1935).

(4) F. J. Glavis, L. L. Ryden and C. S. Marvel, *ibid.*, **59**, 707 (1937).

(5) C. S. Marvel, S. J. Davis and F. J. Glavis, *ibid.*, **60**, 1450 (1938).

(6) C. S. Marvel and W. H. Sharkey, *ibid.*, **61**, 1603 (1939).

known having a mainly head-to-head, tail-to-tail structure.[7] Some evidence has been found by Marvel and Dunlap[8] for a head-to-tail structure in the two-to-one copolymer of vinyl chloride and sulfur dioxide. Kharasch and Friedlander[9] have carried out the photochemical reaction of sulfur dioxide with octene-1 in the presence of bromotrichloromethane which functions as a chain-transfer agent. The molecular weight of the resulting polysulfones could be decreased by increasing the amount of bromotrichloromethane present during the polymerization; when equimolar amounts of the three reactants were irradiated, a compound (III) was obtained having a head-to-tail arrangement of the sulfur dioxide and olefin moieties.



$$BrCH(C_6H_{13})CH_2SO_2CH(C_6H_{13})CH_2CCl_3$$

III

The principal evidence favoring the head-to-head, tail-to-tail structure (II) in olefin–sulfur dioxide copolymers rested on a comparison of the hydrolysis products of the polymers with reference compounds prepared by syntheses involving β-halosulfide intermediates. Since rearrangements *via* the cyclic sulfonium ion[10] are now known to occur in such reactions, this evidence required critical reexamination. In the present investigation, only the propylene–sulfur dioxide copolymer (propylene polysulfone) was studied since the earlier work[3,4] had dealt most intensively with this polymer. Structural evidence presented[4–6] for other polysulfones consisted of certain reactions analogous to those discussed below in connection with the propylene–sulfur dioxide copolymer. As shown below, we have found that two of the reference compounds employed in the original determination of the structure of this copolymer were assigned incorrect structures, and on the basis of the corrected structures, a head-to-tail structure (I) is indicated in the propylene–sulfur dioxide copolymer. By analogy, we believe that other olefin–sulfur dioxide copolymers have a head-to-tail structure.

Propylene polysulfone is cleaved by hot aqueous sodium hydroxide to acetaldehyde and a salt $C_4H_9S_2O_4Na$.[3] We have shown this salt to be sodium 2-methylsulfonyl-1-propanesulfinate (IV), since the compound is converted by treatment with benzyl chloride to a disulfone melting at 114–115° which has been proved to be 1-benzylsulfonyl-2-methylsulfonylpropane (V) by an unequivocal synthesis (Fig. 1). Benzyl 1-propenyl sulfone (VI), prepared by the method of Backer and de Jong,[11] was treated with methanethiol and triethylamine to yield 1-benzylsulfonyl-2-methylmercaptopropane (VII). This intermediate was oxidized by hydrogen peroxide to 1-benzylsulfonyl-2-methylsulfonylpropane (V), which proved to be identical with the disulfone prepared from the propylene polysulfone hydrolysis product. The isomeric disulfone 2-benzylsulfonyl-1-methylsulfonylpropane (VIII), m.p. 160°, was prepared for comparison purposes by addition of α-toluenethiol to methyl 1-propenyl sulfone (XX, *vide infra*), followed by oxidation of the adduct (IX) by hydrogen peroxide.

The salt $C_4H_9S_2O_4Na$ (IV) was also converted by the procedure of Hunt and Marvel[3] *via* the sodium sulfonate $C_4H_9S_2O_5Na$ (X) to a sulfonyl chloride melting at 100°. This compound was shown by us to be 2-methylsulfonyl-1-propanesulfonyl chloride (XI) by an independent synthesis (Fig. 1). Sodium 2-hydroxy-1-propanesulfonate (XII)[12] was converted to sodium 2-bromo-1-propanesulfonate (XIII) by treatment with hydrobromic acid, and the crude intermediate XIII converted to sodium 2-methylmercapto-1-propanesulfonate (XIV) by means of sodium methyl mercaptide. The salt XIV on oxidation by potassium permanganate and treatment with phosphorus pentachloride yielded 2-methylsulfonyl-1-propanesulfonyl chloride (XI). A mixed melting point with the sulfonyl chloride obtained as a derivative of the salt $C_4H_9S_2O_4Na$ (IV) was undepressed; the sulfonyl chlorides from both sources yielded identical anilides melting at 105°.

Hunt and Marvel[3] carried out an intended synthesis of 1-methylsulfonyl-2-propanesulfonyl chloride (XV) and obtained a sulfonyl chloride melting at 100° which was identical to that obtained as a derivative of the degradation product $C_4H_9S_2O_4Na$ from propylene polysulfone. Since our evidence as described above led us to ascribe to this compound the structure XI rather than the structure XV assigned to it by Hunt and Marvel,[3] it was necessary for us to investigate the possibility of rearrangements in the reactions used by these workers.

The studies of Fuson, Price and Burness[10a] led us to expect that the reaction of thionyl chloride with methyl 2-hydroxy-1-propyl sulfide (XVI) would lead to the unrearranged product, methyl 2-chloro-1-propyl sulfide (XVII). This was confirmed experimentally by conversion of the chlorosulfide XVII to methyl 1-propyl sulfone (XVIII) *via* oxidation to methyl 2-chloro-1-propyl sulfone (XIX), dehydrochlorination of the sulfone XIX to methyl 1-propenyl sulfone (XX) and hydrogenation of this unsaturated sulfone (Fig. 1) to give the desired methyl 1-propyl sulfone (XVIII).

However, the reaction of sodium sulfite with methyl 2-chloro-1-propyl sulfide (XVII) was found not to produce sodium 1-methyl-mercapto-2-propanesulfonate (XXI) as believed by Hunt and Marvel[3] but instead yielded the rearranged isomer, sodium 2-methylmercapto-1-propanesulfonate (XIV). The structure of the product was directly proved by Raney nickel hydrogenolysis to sodium 1-propanesulfonate (XXII) which was characterized by comparison of its infrared spectrum with those of authentic samples of sodium 1-propanesulfonate and sodium 2-propanesulfonate.

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[7] C. S. Marvel, E. D. Weil, L. B. Wakefield and C. W. Fairbanks, THIS JOURNAL, **75**, 2326 (1953).

[8] C. S. Marvel and L. H. Dunlap, *ibid.*, **61**, 2709 (1939).

[9] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **13**, 883 (1948).

[10] (a) R. C. Fuson, C. C. Price and D. M. Burness, *ibid.*, **11**, 476 (1946); (b) R. C. Fuson and A. J. Speziale, THIS JOURNAL, **71**, 1582 (1949).

[11] H. J. Backer and G. J. de Jong, *Rec. trav. chim.*, **67**, 884 (1948).

[12] J. M. Stewart and H. P. Cordts, THIS JOURNAL, **74**, 5882 (1952); *cf.* R. Schenck and S. Kaizerman, *ibid.*, **75**, 1636 (1953).

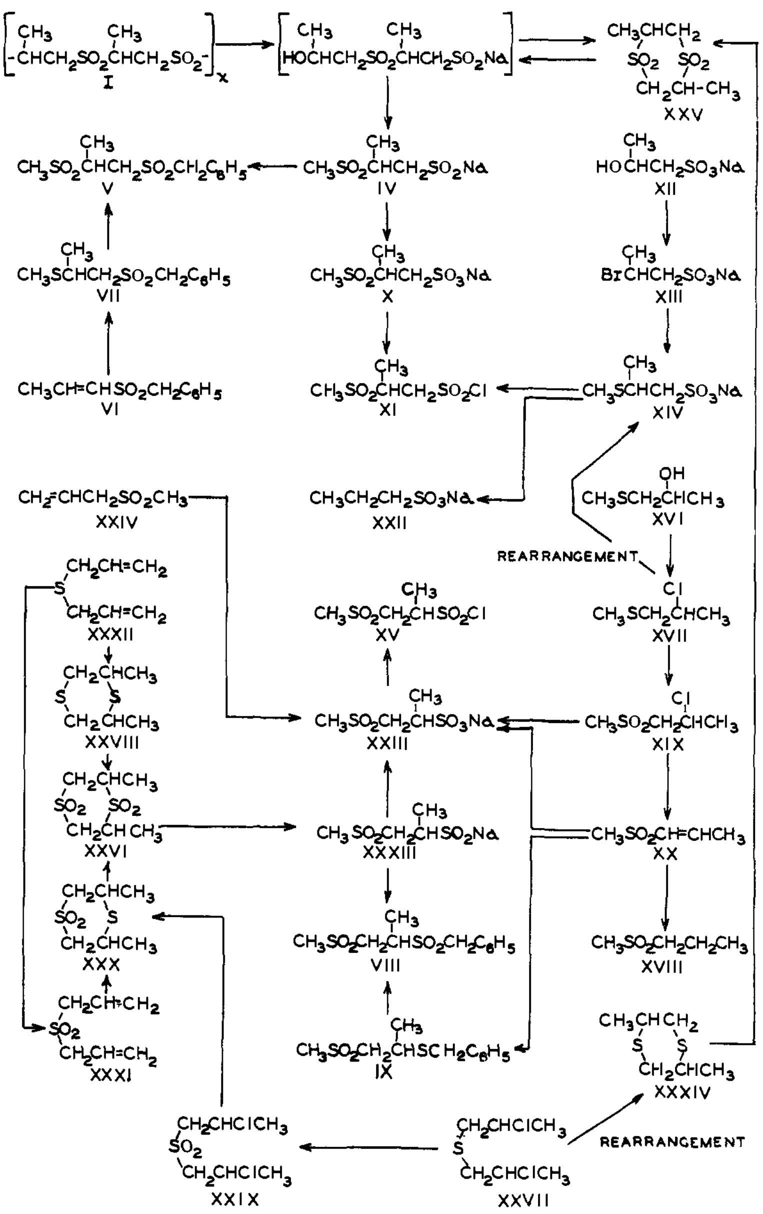

Fig. 1.

The true 1-methylsulfonyl-2-propanesulfonyl chloride (XV) was produced by modifying the above-described synthesis of Hunt and Marvel[3] so as to eliminate the possibility of sulfonium ion rearrangement. Methyl 2-chloro-1-propyl sulfide (XVII) was oxidized to methyl 2-chloro-1-propyl sulfone (XIX) and treated with sodium sulfite to produce sodium 1-methylsulfonyl-2-propanesulfonate (XXIII); this salt upon treatment with phosphorus pentachloride yielded 1-methylsulfonyl-2-propanesulfonyl chloride (XV) which melted at 65°. The same sodium sulfonate XXIII and sulfonyl chloride derivative XV were produced by the base-catalyzed addition of sodium bisulfite to methyl 1-propenyl sulfone (XX) or to methyl allyl sulfone (XXIV)[13] (Fig. 1).

The rearrangement in the reaction of methyl 2-chloro-1-propyl sulfide (XVII) with sodium sulfite may be understood on the basis of a sulfonium ion mechanism.[10] The reactive species present when the chlorosulfide XVII is dissolved in an ionizing solvent is very probably the cyclic sulfonium chloride XVIIa. By analogy with most other bimolecular nucleophilic ring-opening reactions on episulfides and epoxides,[14] the sulfonium ion would be expected to undergo ring-opening by attack of the sulfite anion on the less-substituted carbon, yielding the observed product (Fig. 2).[15] Hunt and Marvel[3] reported the synthesis of 2-methylsulfonyl-1-propanesulfonyl chloride (XI) from sodium 2-bromo-1-propanesulfonate (XIII) which in turn was prepared by the reaction of sodium sulfite with 1,2-dibromopropane. Hunt[16] reported difficulty in repetition of the latter reaction. Since the sulfonyl chloride obtained by this synthesis was reported as melting at 65°, we now believe that the product obtained by Hunt and Marvel was actually 1-methylsulfonyl-2-propanesulfonyl chloride (XV). Our attempts to repeat the preparation of sodium 2-bromo-1-propanesulfonate (XIII) from 1,2-dibromopropane led only to a negligible yield of amorphous product. The work of Clutterbuck and Cohen[17] and Gilta[18] suggests that the reaction should lead to a mixture rather than a single product resulting from displacement of the primary bromine atom.

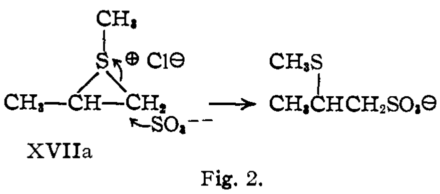

Fig. 2.

Propylene polysulfone dissolves readily in dilute aqueous sodium hydroxide equivalent to one-half of the sulfone linkages present; upon acidification of the solution a high yield of a compound C_6H_{12}-

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[13] H. J. Backer and G. J. deJong, *Rec. trav. chim.*, **70**, 564 (1951), and L. Rothstein, *J. Chem. Soc.*, 684 (1934), have shown that the products obtained by base-catalyzed addition reactions of allyl sulfones are the same as obtained with the corresponding 1-propenyl sulfones.

[14] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 97–99.

[15] A close analogy has been noted[14] between rearrangement reactions of β-halosulfides and β-haloamines, and is further extended by the reaction XVII → XIV reported here. The analogous reaction of 2-bromo-1-propylamine with sodium sulfite to yield the rearrangement product sodium 2-amino-1-propanesulfonate has been reported by P. Rumpf, *Bull. soc. chim.*, [5] **5**, 871 (1938).

[16] M. Hunt, Thesis, Master of Science, University of Illinois, 1935, p. 39.

[17] P. W. Clutterbuck and J. B. Cohen, *J. Chem. Soc.*, **121**, 120 (1922).

[18] G. Gilta, *Bull. soc. chim. Belg.*, **31**, 246 (1922).

S_2O_4, m.p. 332 ± 2°, is obtained.[3,19] Hunt and Marvel[3] assigned to this compound the structure of 2,6-dimethyl-*p*-dithiane 1,1,4,4-tetroxide (XXVI) on the basis of its cleavage by hot sodium hydroxide to yield acetaldehyde and the salt $C_4H_9S_2O_4Na$ which these authors believed to be sodium 1-methylsulfonyl-2-propanesulfinate, identical to that obtained by direct cleavage of propylene polysulfone. Since we have shown this salt to be actually sodium 2-methylsulfonyl-1-propanesulfinate (IV), our present evidence indicates that the disulfone $C_6H_{12}S_2O_4$ obtained from propylene polysulfone is 2,5-dimethyl-*p*-dithiane 1,1,4,4-tetroxide (XXV), a cyclic analog of the head-to-tail polysulfone structure I.

We have established that the supposedly unequivocal synthesis of 2,6-dimethyl-*p*-dithiane 1,1,-4,4-tetroxide (XXVI) by Glavis, Ryden and Marvel[4] yields actually 2,5-dimethyl-*p*-dithiane 1,1,4,4-tetroxide (XXV). These workers treated bis-(2-chloro-1-propyl) sulfide (XXVII) with sodium sulfide to produce a compound which they believed to be 2,6-dimethyl-*p*-dithiane (XXVIII), since no rearrangements in the β-halosulfide series were known at that time. The cyclic disulfide upon oxidation produced the disulfone $C_6H_{12}S_2O_4$ melting at 332 ± 2° and identical to that obtained by degradation of propylene polysulfone. To eliminate the possibility of a sulfonium ion rearrangement at the ring closure step, we oxidized bis-(2-chloro-1-propyl) sulfide (XXVII) to bis-(2-chloro-1-propyl) sulfone (XXIX), then effected the ring closure to 2,6-dimethyl-*p*-dithiane 4,4-dioxide (XXX), and oxidized this intermediate to the disulfone $C_6H_{12}S_2O_4$ which must unequivocally be 2,6-dimethyl-*p*-dithiane 1,1,4,4-tetroxide (XXVI). This product melted at 312–313°, and differed markedly in infrared spectrum from the disulfone (XXV) obtained by degradation of propylene polysulfone. A mixed melting point of the two compounds was depressed to 295–300°.

The disulfone XXVI also has been synthesized by Backer and van der Ley[20] from diallyl sulfone (XXXI) by the base-catalyzed addition of hydrogen sulfide followed by oxidation of the intermediate 2,6-dimethyl-*p*-dithiane 4,4-dioxide (XXX). A third synthesis of the disulfone XXVI has been carried out by us; hydrogen sulfide was added to allyl sulfide (XXXII) in the presence of a basic catalyst (triethylamine) and a free-radical chain inhibitor (pyrogallol) and the intermediate 2,6-dimethyl-*p*-dithiane (XXVIII) was then treated with hydrogen peroxide to produce the disulfone XXVI.

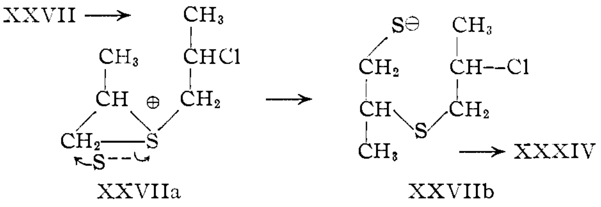
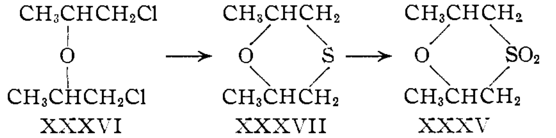


Fig. 3.

The two disulfones (XXV and XXVI) underwent cleavage by hot aqueous sodium hydroxide to yield isomeric products. Whereas the disulfone XXV melting at 332° yielded a salt $C_4H_9S_2O_4Na$ which gave as its derivatives 1-benzylsulfonyl-2-methylsulfonylpropane (V), m.p. 114–115°, and 2-methylsulfonyl-1-propanesulfonyl chloride (XI), m.p. 100°, our synthetic 2,6-dimethyl-*p*-dithiane 1,1,-4,4-tetroxide (XXVI) yielded a sodium salt which gave as derivatives 2-benzylsulfonyl-1-methylsulfonylpropane (VIII), m.p. 159–160°, and 1-methylsulfonyl-2-propanesulfonyl chloride (XV), m.p. 65°. Therefore the salt made by cleaving the disulfone (XXVI) must be the true sodium 1-methylsulfonyl-2-propanesulfinate (XXXIII).

The formation of the rearranged product 2,5-dimethyl-*p*-dithiane (XXXIV) by the reaction of bis-(2-chloro-1-propyl) sulfide (XXVII) with sodium sulfide has been established by the above evidence, and is explainable by the sulfonium ion hypothesis (Fig. 3). The intermediate sulfonium cation XXVIIa undergoes nucleophilic attack at the less-substituted carbon atom of the ring. The intermediate XXVIIb then would be expected to undergo ring closure by intramolecular attack of the negatively-charged sulfur atom upon the chlorine-substituted carbon atom to form a six-membered ring rather than by attack of the uncharged dicovalent sulfur atom upon the chlorine-substituted carbon atom to form a three-membered ring.

Hunt and Marvel[3] observed the formation in low yield of a compound $C_6H_{12}SO_3$ when propylene polysulfone was refluxed for one day with aqueous sodium carbonate. The structure was shown by these workers to be that of 2,6-dimethyl-*p*-oxathiane 4,4-dioxide (XXXV) by synthesis from bis-(1-chloro-2-propyl) ether (XXXVI); this compound was treated with sodium sulfide to produce 2,6-dimethyl-*p*-oxathiane which was then oxidized to the sulfone (XXXV).



We have confirmed the structure of the intermediate (XXXVII) by Raney nickel desulfurization to diisopropyl ether, and have further proved the identity of one geometrical isomer of the synthetic product XXXV with that derived from propylene polysulfone, by comparison of the infrared spectra.

An alternative synthesis of the sulfone XXXV

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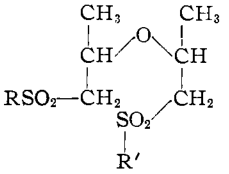
[19] The melting point of this compound has been variously reported as 315°,[2] 320°[3] and 334°.[4] In the present investigation the melting point as taken in a capillary has been found to be indistinct and unreliable. The Maquenne block method, with a cover glass to decrease loss of the sample by sublimation, has permitted us to obtain sharp melting points ranging from 330° to 334° (cor.) with the variation attributable to different rates of heating.

[20] H. J. Backer and R. van der Ley, *Rec. trav. chim.*, **70**, 564 (1951). These workers report a melting point of 320° for their product. By repeating their synthesis we obtained a product melting at 313° (on calibrated thermometer, using either capillary or Maquenne block method); by comparison of infrared spectra we find this product to be identical to that obtained from bis-(2-chloro-1-propyl) sulfone (XXIX) and different from that obtained from the degradation of propylene polysulfone. Our intermediate XXX obtained either from the sulfone XXIX or diallyl sulfone (XXXI) is identical with that described by Backer and van der Ley.

by treatment of diallyl sulfone (XXXI) with an aqueous base has recently been reported by Backer and van der Ley[20] and Ford-Moore,[21] and we have prepared the sulfone XXXV by the reaction of aqueous sodium hydroxide with bis-(2-chloro-1-propyl) sulfone (XXIX). Both the disulfones 2,5-dimethyl-*p*-dithiane 1,1,4,4-tetroxide (XXV) and 2,6-dimethyl-*p*-dithiane 1,1,4,4-tetroxide (XXVI) produce 2,6-dimethyl-*p*-oxathiane 4,4-dioxide (XXXV) in approximately 5% yield upon refluxing with sodium carbonate. The formation of 2,6-dimethyl-*p*-oxathiane 4,4-dioxide (XXXV) from propylene polysulfone was explained by Hunt and Marvel[3] on the basis of the hypothetical "head-to-head, tail-to-tail" structure II which our evidence controverts; these authors proposed bis-(2-hydroxy-1-propyl) sulfone as the intermediate. The formation of 2,6-dimethyl-*p*-oxathiane 4,4-dioxide (XXXV) from the disulfones XXV and XXVI is not explainable on the basis of this intermediate, however. Most significantly, the formation of the sulfone XXXV from the disulfone XXV (which we have proved to have a head-to-tail structure) shows that a head-to-head, tail-to-tail structure of the polymer cannot be inferred from the structure of the cyclic ether-sulfone XXXV.

The alkaline cleavage of the disulfones XXV, XXVI or of propylene polysulfone leads in each case to an initial product having a β-hydroxy-*n*-propylsulfonyl group. The ease with which β-hydroxysulfones undergo base-catalyzed etherification has long been recognized.[22] The second step in the formation of the sulfone XXXV is probably an etherification of this sort. The resulting ether intermediate XXXVIII undergoes ring-closure by a mechanism not yet elucidated.



R,R′ = $CH(CH_3)CH_2SO_2Na$, $-CH_2CH(CH_3)SO_2Na$ or Na

XXXVIII

Since propylene polysulfone has been shown to possess a head-to-tail structure (I), the explanation advanced by Hunt and Marvel to explain the cleavage of the polymer at alternate sulfone linkages no longer is applicable. In terms of the head-to-tail structure, this behavior may be rationalized by reference to the greatly enhanced susceptibility of a γ-disulfone to alkaline cleavage over that of a monosulfone (Stauffer's rule).[23] Following the cleavage of the polymer chain at a sulfone linkage by sodium hydroxide (forming the primary sodium sulfinate and secondary alcohol rather than the secondary sodium sulfinate and primary alcohol[24]), the neighboring sulfone linkages are now deactivated relative to those elsewhere in the chain, since those sulfone linkages not adjacent to a point of cleavage are each located γ- to two labilizing sulfonyl groups.

An alternative preparation of propylene polysulfone was investigated. Propylene sulfide[25] was polymerized by warming with a small amount of sodium ethoxide. If the propagation step of the polymerization proceeds by nucleophilic attack consistently at either the primary or secondary carbon of the episulfide ring, a head-to-tail polymer must result. Ring-opening by attack at the less-hindered carbon has been demonstrated[26] in other reactions of propylene sulfide with nucleophilic reagents; therefore the polymerization very probably proceeds as in Fig. 4.

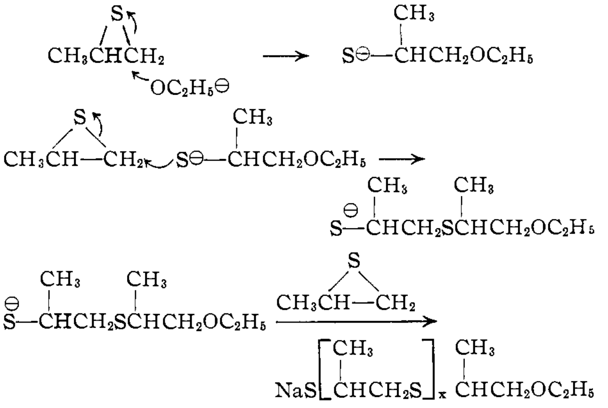


Fig. 4.

Oxidation of a low molecular weight polymer thus prepared, employing excess peracetic acid, yielded a white brittle polymer, insoluble in the common organic solvents, having a decomposition range of 225–230° (the propylene–sulfur dioxide copolymer melts with decomposition at about 250°), and having an infrared spectrum almost identical to that of the propylene–sulfur dioxide copolymer. The propylene polysulfone thus prepared yielded the same cyclic disulfone XXV on alkaline hydrolysis as is obtained from the copolymer. It is therefore indicated that polymerized propylene sulfide and the oxidized polymer therefrom both have a head-to-tail structure.

Experimental[27]

Propylene–Sulfur Dioxide Copolymer.—A procedure based on that of Ryden, Glavis and Marvel[28] was followed. A steel bomb was chilled in a Dry Ice-acetone-bath, and charged with approximately 100 ml. of liquefied propylene, 100 ml. of liquefied sulfur dioxide, 3 ml. of ascaridole and 20 ml. of absolute ethanol. The bomb was sealed and held at 25–30° for one day. Approximately 100 g. of polymer was obtained having the physical and chemical properties previously described.[2,3] The polymer was degraded by the procedures of Hunt and Marvel[3] to a cyclic disulfone $C_6H_{12}S_2O_4$, melting at 332 ± 2°,[19] a cyclic sulfone-ether $C_6H_{12}SO_3$

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[21] A. H. Ford-Moore, *J. Chem. Soc.*, 2433 (1949).

[22] R. Otto, *J. prakt. Chem.*, [2] **30**, 206 (1884); R. Otto and J. Tröger, *Ber.*, **26**, 944 (1893); J. Tröger and C. Budde, *J. prakt. Chem.*, [2] **66**, 130 (1902).

[23] C. M. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 744.

[24] C. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2338 (1929).

[25] French Patent 797,621; *C. A.*, **30**, 7122 (1936).

[26] W. Davies and W. E. Savige, *J. Chem. Soc.*, 317 (1950); H. R. Snyder and W. Alexander, THIS JOURNAL, **70**, 217 (1948).

[27] All melting points reported herein are corrected. The microanalyses were performed by Miss Emily Davis, Mrs. Esther Fett, Mrs. Jean Fortney, Mrs. Katherine Pih and Mr. J. Nemeth of the University of Illinois Microanalytical Laboratory. The authors are indebted to Miss Helen Miklas for the determination of the infrared spectra. The spectra reported in this article were obtained on a Perkin-Elmer model 21 double beam spectrophotometer.

[28] L. L. Ryden, F. J. Glavis and C. S. Marvel, THIS JOURNAL, **59**, 1014 (1937).

melting at 104°, and a salt of $C_4H_9S_2O_4Na$. The same salt was obtained by alkaline hydrolysis of the degradation product $C_6H_{12}S_2O_4$ in the manner described by Hunt and Marvel. The salt was converted as described by these workers to a sulfonyl chloride melting at 100° and a sulfonanilide melting at 105°. A new derivative was also prepared (see below).

2-Methylsulfonyl-1-benzylsulfonylpropane (V) from Sodium 2-Methylsulfonyl-1-propanesulfinate (IV).—Five grams of the dry salt and 5 g. of benzyl chloride (100% excess) in 70 cc. of absolute ethanol were heated overnight in a pressure bottle at 95–100°. The mixture was filtered while hot; the filtrate was concentrated to one-half the original volume, and refrigerated, yielding 3.5 g. (62%) of colorless crystals melting at 113.5–114.5°. Recrystallization from ethanol raised the melting point to 114–115°.

Anal. Calcd. for $C_{11}H_{16}S_2O_4$: C, 47.80; H, 5.83. Found: C, 47.92; H, 5.68.

2-Methylmercapto-1-benzylsulfonylpropane (VII).—Following the procedure of Backer and de Jong,[11] sodium benzylmercaptide and allyl chloride were converted to allyl benzyl sulfide; this compound was oxidized to allyl benzyl sulfone which was isomerized to benzyl 1-propenyl sulfone (VI), m.p. 82–83°, by heating with triethylamine in a sealed tube at 120° for 6 hr. (Backer and de Jong employed triamylamine in this step).

To a chilled mixture of 2 g. of benzyl 1-propenyl sulfone (VI), 15 cc. of triethylamine and 15 cc. of tetrahydrofuran contained in a glass bomb tube was added 5 ml. of liquefied methanethiol; the tube was sealed and heated for 4 hr. at 110°. The mixture was then freed of volatile constituents under reduced pressure and the residual oil induced to crystallize by chilling, yielding 2.2 g. of colorless crystals, m.p. 42–45° (crude). After several recrystallizations from dilute ethanol, the compound melted at 50–51°.

Anal. Calcd. for $C_{11}H_{16}S_2O_2$: C, 54.06; H, 6.60. Found: C, 54.60; H, 6.94.

2-Methylsulfonyl-1-benzylsulfonylpropane (V) from 2-Methylmercapto-1-benzylsulfonylpropane (VII).—To a solution of 1.5 g. of 2-methylmercapto-1-benzylsulfonylpropane (VII) in 5 ml. of glacial acetic acid was added 2 ml. of 30% hydrogen peroxide. After the initial heat of reaction subsided, the mixture was heated for 15 min. on the steam-bath, diluted with several volumes of water, and refrigerated. The product was removed by filtration; 1.5 g. of colorless crystals melting at 112–113.5° (crude) was obtained. Recrystallization from ethanol yielded 1.4 g. of product melting at 114–115° and giving an undepressed mixed melting point with the benzylsulfonyl derivative V obtained from sodium 2-methylsulfonyl-1-propanesulfinate (IV).

1-Methylsulfonyl-2-benzylsulfonylpropane (VIII).—One gram of methyl 1-propenyl sulfone (XX, *vide infra*) and 1.2 g. of α-toluenethiol (Eastman Kodak Co. white label) were refluxed for 3 hr. in 5 ml. of tetrahydrofuran and 5 ml. of triethylamine. The mixture was evaporated under reduced pressure; the residual oil was dissolved in benzene, washed with dilute sodium hydroxide solution and then with water, dried over calcium chloride, and the benzene evaporated leaving 1.3 g. of 1-methylsulfonyl-2-benzylmercaptopropane (IX) as a colorless oil. One-half gram of this crude product was dissolved in 2 ml. of glacial acetic acid and 1 ml. of 30% hydrogen peroxide added. After the initial heat of reaction subsided, the solution was heated for 15 min. on the steam-bath, diluted several-fold with water, and chilled, yielding colorless crystals, m.p. 157–158°. After one recrystallization from 95% ethanol, 0.6 g. of product melting at 160° was obtained.

Anal. Calcd. for $C_{11}H_{16}S_2O_4$: C, 47.80; H, 5.83. Found: C, 48.09; H, 5.84.

Sodium 2-Methylmercapto-1-propanesulfonate (XIV).—Sodium 2-hydroxy-1-propanesulfone (XII) was prepared by the reaction of propylene oxide with sodium bisulfite.[12] Fifty grams of the recrystallized salt was refluxed with 200 ml. of 48% hydrobromic acid for 5 hr., the excess acid then taken off under reduced pressure, and the residue heated at 100° under reduced pressure for several hours. The residue was extracted with boiling methanol; the extracts were treated with decolorizing charcoal, filtered, and refrigerated, yielding 24 g. (35%) of crude sodium 2-bromo-1-propanesulfonate (XIII). Ten grams of this product was heated with 68 ml. of 1.3 *M* sodium methylmercaptide in methanol in a sealed pressure bottle for one day at 95–100°. The mixture was diluted with 100 ml. of ethanol, heated to boiling with decolorizing charcoal, filtered while hot, and chilled in a refrigerator, producing 6.5 g. (76% yield) of sodium 2-methylmercapto-1-propanesulfonate (XIV).

Anal. Calcd. for $C_4H_9S_2O_3Na$: C, 24.99; H, 4.72. Found: C, 24.79; H, 4.50.

2-Methylsulfonyl-1-propanesulfonyl Chloride (XI) from Sodium 2-Methylmercapto-1-propanesulfone (XIV).—The procedure of Hunt and Marvel[3] was followed, employing 5% aqueous potassium permanganate to oxidize the methylmercapto group and phosphorus pentachloride to convert the crude oxidation product to the corresponding sulfonyl chloride, m.p. 100°. The product gave an undepressed mixed melting point with the sulfonyl chloride XI obtained from the polymer cleavage product. The anilides prepared from both sulfonyl chlorides melted at 105° and gave an undepressed mixed melting point. The infrared spectra in Nujol mull of the sulfonyl chlorides from both sources were identical; bands were at 685, 750, 785, 845, 970, 1030, 1100, 1135 (strong), 1165, 1200, 1245, 1290 (strong), 1305 and 1335 cm.$^{-1}$.

1-Methylmercapto-2-propanol (XVI). (A) From 1-Bromo-2-propanol.—The procedure of Hunt and Marvel[3] was followed. From 100 g. of 1-bromo-2-propanol (Eastman white label) and 275 ml. of 2.62 *M* sodium methylmercaptide in methanol was obtained 25 g. (33%) of 1-methylmercapto-2-propanol, boiling at 69–70° (20 mm.), $n^{20}D$ 1.4817.

(B) From **Propylene Oxide.**—Into a chilled steel bomb containing 150 ml. of propylene oxide and 3 ml. of triethylamine was condensed 70 ml. of methanethiol (Eastman white label). The sealed bomb was heated for one hour at 100°, and the product fractionated through a 10″ Fenske column. A nearly quantitative yield of colorless product boiling at 68–69.5° (18 mm.), $n^{20}D$ 1.4823, was obtained. The infrared spectrum showed the product to be identical to that produced by method A. The spectra of both products revealed bands at 705, 755, 770, 820, 875, 940 (strong), 965, 1050 (strong), 1070 (strong), 1130 (strong), 1205, 1250, 1275–1300, 1320, 1350, 1375, 1430 (strong) and 1635 cm.$^{-1}$.

Methyl 2-Chloro-1-propyl Sulfide (XVII).—The procedure of Hunt and Marvel[3] was followed; an improved yield was obtained by the use of purified thionyl chloride and by distillation of the product at a lower pressure. From 20 g. of 1-methylmercapto-2-propanol (XVI) and 26.5 g. of thionyl chloride was obtained 20 g. (84% yield) of product boiling at 47–48° (17 mm.), $n^{20}D$ 1.4851.

Methyl 2-Chloro-1-propyl Sulfone (XIX).—To a stirred solution of 8.7 g. of methyl 2-chloro-1-propyl sulfide (XVII) in 50 ml. of glacial acetic acid was slowly added 17 ml. of 30% hydrogen peroxide. The mixture was kept at 0–10° during the addition, then warmed over several hours to room temperature and finally heated for 15 min. on the steam-bath. After removal of the solvent under reduced pressure, the product was distilled, boiling at 97–100° (0.4 mm.) with slight decomposition, $n^{20}D$ 1.4830–1.4814, yield 7 g. of nearly-colorless liquid.

Anal. Calcd. for $C_4H_9SO_2Cl$: C, 30.67; H, 5.79. Found: C, 30.99; H, 5.88.

Methyl 1-Propenyl Sulfone (XX).—Fifty grams of methyl 2-chloro-1-propyl sulfone (XIX) was shaken for one day with 32 g. of triethylamine in 500 ml. of dry benzene. The mixture was filtered removing thereby 40 g. (92% of the theoretical) of triethylamine hydrochloride, and the filtrate was evaporated under reduced pressure. The residual oil was fractionated through an 8-in. Fenske column, yielding 26 g. (68% yield) of colorless distillate boiling at 93.5–95° (2.8 mm.). The product crystallized on standing and after recrystallization from ligroin melted at 40.5–41°.

Anal. Calcd. for $C_4H_8SO_2$: C, 39.98; H, 6.71. Found: C, 39.80; H, 6.67.

Hydrogenation of Methyl 1-Propenyl Sulfone (XX).—One gram of methyl 1-propenyl sulfone (XX), m.p. 40.5–41°, in 25 ml. of absolute ethanol was shaken for 8 hr. at room temperature in the presence of commercial Raney nickel catalyst under four atmospheres of hydrogen. The mixture was filtered, evaporated, and the residual oil distilled, yielding 0.5 g. of colorless oil boiling at 135° (20 mm.). The infrared spectrum in 5% chloroform solution of this compound was identical to that of authentic methyl 1-propyl sulfone (XVIII)[29]; absorption bands were found at 865, 960 (strong), 1075, 1095, 1145 (strong), 1215, 1255, 1295, 1320 (strong), 1350, 1390, 1420 and 1465–1475 cm.$^{-1}$.

Reaction of Methyl 2-Chloro-1-propyl Sulfide (XVII) with Sodium Sulfite.—The reaction described by Hunt and Marvel[3] was repeated. From 10 g. of methyl 2-chloro-1-propyl sulfide (XVII) and 11.2 g. of sodium sulfite was obtained 3 g. of colorless crystalline salt which was converted in the manner described by these authors by oxidation with potassium permanganate and treatment with phosphorus pentachloride to a sulfonyl chloride melting at 100°. A mixed melting point with 2-methylsulfonyl-1-propanesulfonyl chloride (XI) derived from the cleavage product IV of propylene polysulfone was undepressed.

Three grams of the sodium salt XIV produced as described above was refluxed for 4 hr. with 25–30 g. of freshly-prepared Raney nickel "C"[30] in 100 ml. of absolute ethanol, filtered while warm, evaporated, and the residue recrystallized from 95% ethanol yielding 1.1 g. of colorless needles. Comparison of the infrared spectrum (in Nujol mull) of the thoroughly-dried product with the spectra of sodium 1-propanesulfonate and sodium 2-propanesulfonate showed the hydrogenolysis product to be the former compound.

The hydrogenolysis product and the reference sample of sodium 1-propanesulfonate revealed absorption bands at 725, 745, 790–795, 1065 (strong), 1190 (strong), 1200–1210 (strong), 1230 (strong), 1270 and 1300 cm.$^{-1}$. The reference sample of sodium 2-propanesulfonate had bands at 720 (strong), 890, 1045 (strong), 1075, 1165, 1185 (strong), 1210 (strong) and 1290 cm.$^{-1}$.

Reaction of Methyl 2-Chloro-1-propyl Sulfone (XIX) with Sodium Sulfite.—The procedure employed by Hunt and Marvel[3] for the reaction between methyl 2-chloro-1-propyl sulfide (XVII) and sodium sulfite was followed. The resulting salt was converted to the sulfonyl chloride (XV), m.p. 53-60° (crude) in an over-all yield of 20%. The product contained a persistent impurity and numerous recrystallizations were required to raise the melting point to 65°. An infrared curve run on the crude product in Nujol mull showed this to be identical, except for additional weak bands due to an impurity, to 1-methylsulfonyl-2-propanesulfonyl chloride (XV), m.p. 65°, obtained from the methyl 1-propenyl sulfone–sodium bisulfite adduct (see below).

The absorption bands characteristic of pure 1-methylsulfonyl-2-propanesulfonyl chloride (XV) in Nujol mull were found at 690, 710 (strong), 800, 860, 915, 1020, 1075, 1115, 1145 (strong), 1170, 1235 (strong), 1280, 1310 (strong) and 1340 cm.$^{-1}$ (strong).

Sodium 1-Methylsulfonyl-2-propanesulfonate (XXIII) and 1-Methylsulfonyl-2-propanesulfonyl Chloride (XV) from Methyl Allyl Sulfone (XXIV).—Methyl allyl sulfone[31] (XXIV), observed b.p. 129–130° (14 mm.), $n^{20}\text{D}$ 1.4725, was prepared in 66% yield by oxidation of methyl allyl sulfide[32] with 30% hydrogen peroxide by a procedure similar to that used by Backer and van der Ley[20] to prepare diallyl sulfone. To a solution of 2.08 g. (0.02 mole) of sodium bisulfite in 10 ml. of water was added 2.4 g. of methyl allyl sulfone (XXIV) (0.02 mole) and 5 ml. of triethylamine. The mixture was refluxed for 4 hr., then evaporated under reduced pressure, the residue taken up in boiling ethanol and filtered while hot. Upon refrigeration of the filtrate, 3.5 g. of colorless crystals was deposited (80% of the theoretical).

The sulfonyl chloride was prepared by treating the above product with phosphorus pentachloride by the procedure of Hunt and Marvel[3]; the melting point of the product was 65°.

Anal. Calcd. for $C_4H_9S_2O_4Cl$: Cl, 16.09. Found: Cl, 15.92.

Sodium 1-Methylsulfonyl-2-propanesulfonate (XXIII) and 1-Methylsulfonyl-2-propanesulfonyl Chloride (XV) from Methyl 1-Propenyl Sulfone (XX).—The procedure described above was followed, using methyl 1-propenyl sulfone (XX), m.p. 40–41° in place of methyl allyl sulfone (XXIV). An exothermic reaction ensued upon mixing the reagents, and the mixture was refluxed for only one hour. The sodium sulfonate XXIII was isolated in 90% yield and was converted by the above procedure to the sulfonyl chloride XV, m.p. 65°; the mixed melting point with the sulfonyl chloride derived from methyl allyl sulfone (XXIV) was also 65°.

Treatment of 1,2-Dibromopropane with Sodium Sulfite.—An unsuccessful attempt was made to repeat the preparation of sodium 2-bromo-1-propanesulfonate (XIII) as described by Hunt and Marvel.[3] Evaporation of the reaction mixture left a residue only slightly soluble in hot ethanol. No crystalline compound was deposited upon refrigeration of the alcohol extracts.

Bis-(2-chloro-1-propyl) Sulfide (XXVII).—Bis-(2-hydroxy-1-propyl) sulfide was obtained either from propylene oxide and hydrogen sulfide[33] or from propylene α-chlorohydrin and sodium sulfide,[34] the former method being found more convenient. This compound was converted to bis-(2-chloro-1-propyl) sulfide (XXVII) by treatment with concentrated hydrochloric acid by the procedure of Coffey[34] yielding 72% of the theoretical amount, boiling at 95–97° (4.5 mm.). Fuson, Price and Burness[10a] have demonstrated the structural identity of the compound thus prepared with that produced by the reaction of propylene and sulfur monochloride.

Using pure bis-(2-chloro-1-propyl) sulfide (XXVII) prepared as described, the reaction sequence of Glavis, Ryden and Marvel[4] was repeated, the step XXVII → XXXIV proceeding in 15% yield and the step XXXIV → XXV in 95% yield. The identity of the product XXV with the disulfone of m.p. 332° obtained from propylene polysulfone was confirmed by comparison of the infrared spectra in Nujol mull. Both spectra revealed bands at 670 (strong), 720 (weak), 790 (strong), 880 (strong), 910, 1015 (strong), 1065, 1105 (strong), 1130 (strong), 1170 (strong), 1260 (strong), 1275, 1290, 1305 (strong) and 1330 cm.$^{-1}$.

Bis-(2-chloro-1-propyl) Sulfone (XXIX).—This compound was prepared by the procedure of Fuson, Price and Burness.[10a] From 7.5 g. of bis-(2-chloro-1-propyl) sulfide (XXVII) and 13.5 ml. of 30% hydrogen peroxide was obtained 6.4 g. of recrystallized sulfone XXIX melting at 43–44°. Repeated crystallizations ultimately yielded a product melting at the temperature reported by Fuson, *et al.* (56°) but this latter compound doubtless represents only one of the two expected diastereoisomers.

2,6-Dimethyl-*p*-dithiane 4,4-Dioxide (XXX). A. From Diallyl Sulfone (XXXI).—The procedure of Backer and van der Ley[20] was followed. From 11.7 g. (0.08 mole) of diallyl sulfone (XXXI) and 24 g. (0.10 mole) of sodium sulfide monohydrate, 6 g. was obtained of a product melting at 130–140° and consisting probably of *cis–trans* isomers. After repeated recrystallizations from benzene–ligroin mixture, the less-soluble isomer was obtained, melting at 146° as reported by Backer and van der Ley.

B. From Bis-(2-chloro-1-propyl) Sulfone (XXIX).—A solution of 4.4 g. (0.02 mole) of bis-(2-chloro-1-propyl) sulfone (XXIX), m.p. 43–44°, in 25 ml. of absolute ethanol was added dropwise with stirring over one hour to 50 ml. of refluxing 0.46 *M* sodium sulfide in absolute ethanol. The mixture was refluxed for 8 hr., filtered, and evaporated under reduced pressure leaving a mixture of crystals and oil. The residue was washed by decantation with water, and the crystals separated from the remaining oil by filtration. After recrystallization from benzene–ligroin mixture, the crystals melted at 146°.

2,6-Dimethyl-*p*-dithiane 1,1,4,4-Tetroxide (IVb). A. From 2,6-Dimethyl-*p*-dithiane 4,4-Dioxide (XXX).—A solution of 0.2 g. of 2,6-dimethyl-*p*-dithiane 4,4-dioxide (XXX) (prepared by method A or B) in 1 ml. of glacial acetic acid was heated for 15 min. on the steam-bath, the mixture was diluted with 5 ml. of water, cooled, and filtered. The crystals were washed with water and ethanol, and, after recrystallization from nitromethane, dioxane or dimethylformamide, melted at 312–313°. The melting point could not be raised above 313° by repeated recrystallization.[35] Infrared spectra showed that the same product was obtained

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(29) D. T. Allan, T. V. Cullum, R. A. Dean and F. A. Fidler, THIS JOURNAL, **73**, 3630 (1951).

(30) C. D. Hurd and B. Rudner, *ibid.*, **73**, 5158 (1951).

(31) L. Rothstein, *J. Chem. Soc.*, 684 (1934).

(32) J. Obermeyer, *Ber.*, **20**, 2925 (1887); sodium methylmercaptide was employed in place of the lead methylmercaptide used by this worker with similar results.

(33) A. H. Williams and F. N. Woodward, *J. Chem. Soc.*, 38 (1948).

(34) S. Coffey, *ibid.*, **119**, 94 (1921); A. Dewael, *Bull. soc. chim. Belg.*, **39**, 87 (1930).

(35) Backer and van der Ley[20] report a melting point of 320° for this compound. Our melting point was obtained on a Maquenne block using a calibrated thermometer and also checked using a sealed capillary and a Bureau of Standards Anschütz thermometer.

using either the isomer of XXX melting at 146° or the mixture of isomers obtained in methods A or B. The spectra (in Nujol mull) revealed bands at 665, 715 (strong), 800, 885, 920, 930 (weak), 1015, 1035, 1055, 1075 (weak), 1110 (strong), 1135 (strong), 1150, 1185, 1270, 1300 (strong), 1310 (strong) and 1345 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{12}S_2O_4$: C, 33.95; H, 5.70. Found: C, 34.06; H, 5.75.

B. **From Diallyl Sulfide (XXXII)** *via* **2,6-Dimethyl-*p*-dithiane (XXVIII).**—A mixture of 28 g. of diallyl sulfide (XXXII) (Edwal Laboratories), 35 g. of triethylamine and 1 g. of pyrogallol was refluxed for 18 hr. while a slow stream of hydrogen sulfide was introduced. The mixture was then fractionated through an 8″ Vigreux column, yielding 22 g. of unreacted diallyl sulfide (XXXII) distilling at 38–40° (15 mm.), and 1.5 g. of 2,6-dimethyl-*p*-dithiane (XXVIII) distilling at 80–100° (15 mm.), n^{20}D 1.5324 (20% yield based on unrecovered diallyl sulfide). One-tenth gram of the crude dithiane was mixed with 1 ml. of 30% hydrogen peroxide and 1 ml. of glacial acetic acid. After the initial heat of reaction subsided, the solution was heated on the steam-bath for 15 min., diluted with water, cooled, and filtered. A nearly quantitative yield of the disulfone XXVI melting at 312–313° was obtained. A mixed melting point with the disulfone XXVI obtained by procedure A was undepressed.

The disulfone XXVI gave a depressed mixed melting point (295–300°) with the disulfone XXV of melting point 332° derived from propylene polysulfone. The infrared spectra of the two compounds were distinctly different (see above). Attempts to interconvert the compounds were unsuccessful; both were recovered unchanged after sublimation at atmospheric pressure, refluxing with quinoline or triethylamine–dimethylformamide mixture, or heating for three days at 120° in tributylamine. The final proof that the compounds are structural isomers rather than *cis–trans* isomers was furnished by their cleavage reactions (*vide infra*).

Alkaline Cleavage of 2,6-Dimethyl-*p*-dithiane 1,1,4,4-Tetroxide (XXVI).—Three grams of the disulfone XXVI, m.p. 312–313°, was refluxed for 8 hr. with 35 ml. of 10% aqueous sodium hydroxide solution into which a slow stream of nitrogen was passed. The odor of acetaldehyde was evident during this time and the presence of this compound was confirmed by passing the effluent gas into a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. The precipitate after recrystallization from methanol melted at 164–164.5° and gave an undepressed mixed melting point with an authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone[36] prepared in the same way.

The reaction mixture was treated with excess sodium bicarbonate, evaporated dry under reduced pressure, and extracted with 50 ml. of hot absolute ethanol. To the filtered extract containing the cleavage product (sodium 1-methylsulfonyl-2-propanesulfinate) (XXXIII)) was added 12.6 g. (0.1 mole) of benzyl chloride, and the solution heated overnight at 95–100° in a sealed pressure bottle. The reaction mixture was filtered while hot, and the filtrate refrigerated, yielding 1.1 g. of colorless crystals, melting at 148–156° (crude), 159–160° after several recrystallizations from 95% ethanol. A mixed melting point with authentic 1-methylsulfonyl-2-benzylsulfonylpropane (VIII) (see above) was undepressed.

The cleavage reaction of 2,6-dimethyl-*p*-dithiane 1,1,4,4-tetroxide (XXVI) was repeated and an unsuccessful attempt made to obtain the sodium 1-methylsulfonyl-2-propanesulfinate (XXXIII) in analytically pure condition. The cleavage product, however, was converted by the procedure of Hunt and Marvel[3] to the corresponding sulfonyl chloride XV which melted at 65°. Undepressed mixed melting points were obtained with authentic 1-methylsulfonyl-2-propanesulfonyl chloride (XV) derived *via* sodium 1-methylsulfonyl-2-propanesulfonate (XXIII) from methyl allyl sulfone (XXIV), methyl 1-propenyl sulfone (XX) or methyl 2-chloro-1-propyl sulfone (XIX).

2,6-Dimethyl-*p*-oxathiane (XXXVII) and 2,6-Dimethyl-*p*-oxathiane 4,4-Dioxide (XXXV).—The preparation of 2,6-dimethyl-*p*-oxathiane (XXXVII) was carried out by the procedure of Hunt and Marvel.[3] The product was fractionated through a 5″ Vigreux column and boiled at 160–161°, n^{20}D 1.4733.

To 25 ml. of 40% peracetic acid was slowly added 2.5 ml. of the above product. When the heat of reaction subsided, the mixture was warmed briefly to 90° on the steam-bath, poured into excess sodium carbonate solution, and extracted with ether which was dried over sodium sulfate and evaporated. The residual crystals were subjected to fractional crystallization from ligroin, yielding two compounds, one of m.p. 104.5–105.5° identical to the product obtained by degradation of propylene polysulfone by sodium carbonate (as shown by infrared and mixed melting point), and an isomer, m.p. 92.5–93°, which is previously unreported. A mixture of the two isomers melted at 70–88°.

Anal. Calcd. for $C_6H_{12}SO_3$: C, 43.90; H, 7.32. Found: C, 44.16; H, 7.52.

Hydrogenolysis of 2,6-Dimethyl-*p*-oxathiane (XXXVII).—Two grams of 2,6-dimethyl-*p*-oxathiane (XXXVII) and 25 g. of fresh Raney nickel "C"[29] in 100 ml. of diethyl carbitol were stirred and heated at 94–100° for 20 hr., 100 ml. of water added, and the mixture fractionated through a 12-inch Fenske column. The first 10 ml. of distillate was saturated with potassium chloride; the organic layer was separated and redistilled in a micro-still yielding 0.5 g. of diisopropyl ether, b.p. 69°, n^{20}D 1.3713, confirmed by comparison of its infrared spectrum with that of an authentic specimen; both revealed bands at 795, 900, 1010 (strong), 1050, 1100 (strong), 1110 (strong), 1140, 1150 (strong), 1255, 1330, 1365 (strong), 1375 (strong), 1405, 1425, 1450 and 1460 cm.$^{-1}$ (strong).

2,6-Dimethyl-*p*-oxathiane 4,4-Dioxide (XXXV) from Bis-(2-chloro-1-propyl) Sulfone (XXIX).—Five grams of bis-(2-chloro-1-propyl) sulfone (XXIX) was refluxed for 2 hr. with 75 ml. of 2 *N* sodium hydroxide solution. The solution was acidified with dilute hydrochloric acid and extracted with chloroform. The extracts on evaporation yielded 3.5 g. of crude product which was recrystallized from ligroin several times yielding 2 g. of the sulfone XXXV, m.p. 102–103°.

2,6-Dimethyl-*p*-oxathiane 4,4-Dioxide (XXXV) from Diallyl Sulfone (XXXI).—By treating diallyl sulfone (XXXI) with hot aqueous sodium hydroxide according to the procedure of Backer and van der Ley[20] a product melting at 102.5–103.5° was obtained. By means of mixed melting points and infrared measurements this product was proved identical to the sulfone-ether XXXV obtained from propylene polysulfone or from bis-(2-chloro-1-propyl) sulfone (XXIX). The infrared spectrum of 2,6-dimethyl-*p*-oxathiane 4,4-dioxide (XXXV) in Nujol mull revealed bands at 725, 740, 795 (strong), 830, 855 (strong), 900 (strong), 910, 975, 1045–1055 (strong), 1100, 1125–1135 (strong), 1160, 1180, 1205 (strong), 1240, 1270, 1295 (strong) and 1325 cm.$^{-1}$ (strong).

Degradation of 2,5-Dimethyl-*p*-dithiane 1,1,4,4-Tetroxide (XXV) and 2,6-Dimethyl-*p*-dithiane 1,1,4,4-Tetroxide (XXVI) by Sodium Carbonate.—By following the procedure which Hunt and Marvel[3] used in the degradation of propylene polysulfone by sodium carbonate, approximately 5% yields of 2,6-dimethyl-*p*-oxathiane 4,4-dioxide (XXXV) were obtained from either of the two isomeric disulfones. The product was identified by melting point and mixed melting point with that obtained by degradation of the polysulfone.

Polymerization of Propylene Sulfide.—Three milliliters of freshly-redistilled propylene sulfide,[25] b.p. 73–74°, and two drops of 20% ethanolic sodium ethoxide were heated for 2 hr. at 95–100° in a glass pressure bottle. The viscous product was dissolved in chloroform and reprecipitated by addition to methanol, triturated with methanol, again dissolved in chloroform, and reprecipitated by addition to ether. After drying under reduced pressure, 2.5 g. of white tacky resin was obtained.

The polymer could be obtained as a white non-tacky powder by carrying out the polymerization in dioxane solution.

Oxidation of Polymerized Propylene Sulfide.—The purified product from the bulk polymerization of 3 g. of propylene sulfide was dissolved in a mixture of 20 ml. of chloroform and 20 ml. of glacial acetic acid, the mixture heated to boiling on the steam-bath, and 20 ml. of 40% peracetic acid (Buffalo Electrochemical Co.) was cautiously added in small portions over one hour. A white granular precipitate was produced. The mixture was diluted with water, filtered, and the product washed with water, methanol, and ether. After drying over phosphoric anhydride in a vacuum

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[36] H. H. Strain, THIS JOURNAL, 57, 760 (1935).

2.5 g. of white powder, melting with decomposition at 225–230° and insoluble in the common organic solvents, was obtained. The infrared spectrum of this product was found to be nearly identical to that of the propylene–sulfur dioxide copolymer.

The copolymer in Nujol mull revealed bands at 745 (shoulder), 760, 790, 845, 1015, 1075, 1130 (strong), 1230 and 1305–1320 cm.$^{-1}$ (strong); the polysulfone produced by oxidation revealed bands at 745 (broad), 790, 845, 1010, 1075, 1130 (strong), 1230 and 1300–1320 cm.$^{-1}$ (strong).

A sample of the oxidized polymer was prepared for analysis by drying in an Abderhalden pistol at 100°.

Anal. Calcd. for $[C_3H_6SO_2]_x$: C, 33.95; H, 5.70. Found: C, 32.16; H, 5.98.

To 1.50 ml. of 1.15 *N* sodium hydroxide solution was added 0.35 g. of the oxidized polymer. Most of the material went into solution rapidly; the solution was filtered, acidified to congo red with 2 *N* hydrochloric acid, and allowed to stand for two days. Upon filtration, 0.11 g. of crystalline product was obtained, melting at 329° (crude) and identical in its infrared spectrum to the disulfone (XXV) obtained from the propylene–sulfur dioxide copolymer.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Molecular Compounds. I. Picryl Chloride–Hexamethylbenzene in Chloroform Solution

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The equilibrium constant for complex formation in chloroform between picryl chloride and hexamethylbenzene has been determined by a spectroscopic method and a method based on determinations of reaction rates. The latter method gives a value for *K* which is more than ten times larger than the spectroscopic value of 0.073 ± 0.009 liter × mole^{-1}. The spectroscopic value is taken as a measure of the complexing due to the formation of a charge-transfer type intermolecular bond. The latter value measures, in addition to this type of complexing, the sum of all those interactions which can, in any manner, affect the rate of the reaction between picryl chloride and triethylamine.

Picryl chloride and hexamethylbenzene react to form orange-yellow, orthorhombic crystals of a 1:1 molecular compound. This complex has been the subject of extensive investigations, all in the solid state. Powell and Huse[1] have studied the crystal structure by Patterson analyses and general space group considerations and have shown that the crystal consists of alternate layers of picryl chloride and hexamethylbenzene molecules almost parallel to (100) and equally spaced at 3.5Å., although there are observed local disorder structures. Nakamoto[2] has measured the dichroism of this complex and demonstrated that "for the first bands which are supposed to consist of absorptions principally due to π-electrons and the substituents of the benzene rings, the absorption with the electric vectors vibrating perpendicular to the ring plane are always bathochromic and hyperchromic to the absorptions with those vibrating parallel to it." From this it is concluded that the compound results from overlapping of the π-electron clouds in the perpendicular direction between benzene layers. These results support the quantum-mechanical theory of molecular compound formation recently presented by Mulliken,[3] who has extended the previous hypotheses of Weiss,[4] Woodward[5] and Brackmann[6] on molecular compound formation and presented them in a more general and more accurate form.

Our own interest is in the properties of molecular compounds in solution. In this paper we wish to report the results of measurements of the equilibrium constant of the picryl chloride–hexamethylbenzene compound in chloroform solution by a spectroscopic method and by a method involving reaction rate determinations.

Absorption Spectra Studies.—The formation of a molecular compound is in many cases accompanied by the appearance of strong color, and advantage may be taken of this phenomenon to determine the equilibrium constant for compound formation. The spectroscopic method has been used by Landauer and McConnell[7] to determine the equilibrium constants and absorption spectra of the aromatic amine–polynitrohydrocarbon complexes and by Keefer and Andrews[8] to study the interaction of iodine and bromine with organic halides.

Following these latter authors,[8] we define the equilibrium constant for complex formation as

$$K = \frac{(\mathrm{PH})}{(\mathrm{P})(\mathrm{H})} \qquad (1)$$

where (PH), (P) and (H) are the molar equilibrium concentrations of the molecular compound, picryl chloride and hexamethylbenzene, respectively, and assume that, at any wave length

$$d_{\mathrm{PH}} = d - (\mathrm{P})\epsilon_{\mathrm{P}}l - (\mathrm{H}) \qquad \epsilon_{\mathrm{H}}l = \mathrm{PH}\epsilon_{\mathrm{PH}}l \quad (2)$$

where d is the measured optical density, d_{PH}, the optical density due to the molecular compound, l, the light path in cm. and ϵ_{P}, ϵ_{H} and ϵ_{PH} are the extinction coefficients of picryl chloride, hexamethylbenzene and the complex, respectively. Keefer and Andrews have used these two expressions in the form

$$\frac{A}{d_{\mathrm{PH}}} = \frac{1}{K\epsilon_{\mathrm{PH}}} \times B + \frac{1}{\epsilon_{\mathrm{PH}}} \qquad (3)$$

where A and B represent, respectively, $(\mathrm{P})_0(\mathrm{H})_0/(\mathrm{P})_0 + (\mathrm{H})_0 - (\mathrm{PH})$ and $1/(\mathrm{P})_0 + (\mathrm{H})_0 - (\mathrm{PH})$ and where $(\mathrm{P})_0$ and $(\mathrm{H})_0$ represent molar concentrations

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(1) H. M. Powell and G. Huse, *Nature*, **144**, 77 (1939); *J. Chem. Soc.*, 435 (1943).

(2) K. Nakamoto, THIS JOURNAL, **74**, 1739 (1952); see also R. Tsuchida, M. Kobayashi and K. Nakamoto, *Nature*, **167**, 726 (1951).

(3) R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

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