

249 $m\mu$ (ϵ 8400). The infrared spectrum showed a strong band at 1690 cm^{-1} and two medium bands at 3125 and 3220 cm^{-1} .

The basic solution, from which X had been removed, was acidified with 10% hydrochloric acid, and the resulting precipitate (150 mg.) was separated. Fractional crystallization of this acidic product from acetic acid-water gave two isomeric 1,12-dimethyl-1-carboxy-1,2,3,4,9,10,11,12-octa-hydrophenanthrenes (XI).

Anal. Calcd. for $C_{17}H_{22}O_2$ (acid, m.p. 205–207°): C, 79.03; H, 8.58. Found: C, 78.97; H, 9.05.

The ultraviolet spectrum of this acid showed maxima at 265 $m\mu$ (ϵ 440) and 272 $m\mu$ (ϵ 404).

Anal. Calcd. for $C_{17}H_{22}O_2$ (acid, m.p. 186–187°): C, 79.03; H, 8.58. Found: C, 78.73; H, 8.55.

The ultraviolet spectrum of this acid showed maxima at 265 $m\mu$ (ϵ 478) and 272 $m\mu$ (ϵ 440). The infrared spectra of the two acids were almost identical and were similar to the spectrum of dehydroabiatic acid.

The Cyclization of VII (R = Isopropyl).—The cyclization of VII (R = isopropyl, 14.5 g., 0.046 mole) was carried out under conditions identical to those described above for VII (R = H). The product (10 g., 70% yield, m.p. 239–241° (crude) or 242–243.5° pure) was shown to be identical to VIII, obtained from VII (R = H) by: (1) comparison of ultraviolet and infrared spectra, (2) mixed melting point studies, (3) composition, (4) reduction (Wolff-Kishner) to the same three products originally obtained from VII (R = H).

Reaction of Dehydroabiatic Acid with Aluminum Chloride.—A solution of dehydroabiatic acid (2 g., 0.0067 mole, m.p. 171°, λ_{265}^{max} $m\mu$ (ϵ 682), λ_{272}^{max} (ϵ 722)) in thiophene-free benzene (30 ml.) was added, with stirring, to a suspension of freshly sublimed aluminum chloride (2.7 g., 0.02 mole) in thiophene-free benzene (50 ml.). The mixture was heated (reflux) and stirred for three hours, and then stirred at room temperature for one hour. The reaction mixture was hydrolyzed with ice and hydrochloric acid, and the benzene layer was separated and extracted with 5% aqueous sodium hydroxide. The basic solution was acidified and extracted with ether. The oily acid obtained from the ether extract was sublimed (0.1 mm.) to give a white glass, which eventually crystallized. Fractional crystallization of this solid

gave a small amount of a pure compound as colorless plates melting at 159–160°.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58; neut. equiv., 258. Found: C, 79.07; H, 8.61; neut. equiv., 260.

The infrared spectrum of this isomer was quite similar to the acids obtained from VIII. The band in the carbonyl region was at 1700 cm^{-1} . The ultraviolet spectrum was almost identical to the acids obtained from VIII, and showed maxima at 265 $m\mu$ (ϵ 422) and at 272 $m\mu$ (ϵ 413).

The acidic residue obtained, after the 159–160° isomer had been removed, melted over a range of 125–135°. Attempts to obtain a second pure product by recrystallization (methanol-water or petroleum ether) and chromatography (silica gel) failed. A mixture of isomers (m.p. 138–140° with sublimation starting at 136°) was obtained from the chromatogram.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.70; H, 8.88.

Reaction of VII (R = Isopropyl) with Polyphosphoric Acid.—A mixture of polyphosphoric acid (prepared from 24.9 g. of phosphorus pentoxide in 16 ml. of 85% orthophosphoric acid) and VII (R = isopropyl, 1.5 g.) was heated on a steam-bath for two hours. The reaction mixture was poured onto ice and water and the amorphous solid that precipitated was removed by filtration. The solid darkened rapidly to a brown gummy substance when exposed to air. This material was dissolved in ether and extracted with 200 ml. of 5% aqueous sodium hydroxide and 100 ml. of water. No product was obtained from the alkaline extracts. The ether solution contained 1.0 g. of residual oil which solidified after standing for three days. The product melted at 95.5–96.5° after recrystallization from ethanol-water.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16; sapon. equiv., 296. Found: C, 81.24; H, 8.33; sapon. equiv., 290.

The infrared and ultraviolet spectra of this product, which has been assigned structure XII, are discussed in the text of this report.

Acknowledgment.—The authors would like to thank Dr. Stuart W. Fenton for discussions concerning the infrared spectra.

MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

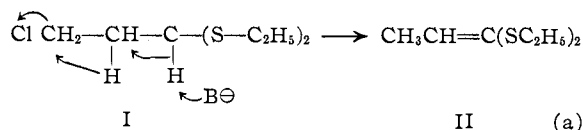
Heterocyclic Vinyl Ethers. VIII.¹ The Acid-catalysed Reaction of α -Haloacetals with Mercaptans

BY WILLIAM E. PARHAM, JACK HEBERLING² AND HANS WYNBERG

RECEIVED AUGUST 4, 1954

The spontaneous loss of hydrogen halide (ϵ -1 elimination) from α -halomercaptans ($R-\overset{X}{\underset{|}{\text{C}}}-\text{CH}(\text{SR})_2$) has been shown to result in the formation of 1,2-bis-(alkylmercapto)-ethylenes ($R-\text{S}-\text{CR}=\text{CH}-\text{S}-R$). There is no unequivocal evidence that ketenemercaptans are formed directly in such reactions. A new synthesis for heterocyclic vinyl sulfides is reported. The compound previously reported to be acrolein diethylmercaptal (III) has been shown to be 1,3-bis-(ethylmercapto)-propene-1 (IV).

Rothstein³ has postulated that the formation of 1,1-bis-(ethylmercapto)-propene-1 (II), by reaction of β -chloropropionaldehyde diethylmercaptal (I) with alkali, occurs as shown in equation (a).

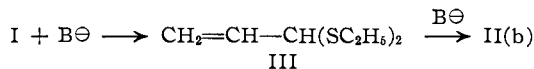


(1) This work was sponsored by the Office of Ordnance Research, Contract No. DA-11-022-ORD-571.

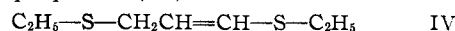
(2) From the Ph.D. Thesis of Jack Heberling, University of Minnesota, 1954.

(3) E. Rothstein, *J. Chem. Soc.*, 1550 (1940).

An alternate reaction path, shown in equation (b), was rejected on the basis that acrolein diethylmercaptal was not isomerized by action of alkali. A

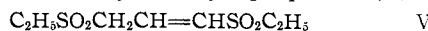


re-examination of the structure of the product previously designated by Rothstein as acrolein diethylmercaptal (III) has now been made, and it is believed that this product is actually 1,3-bis-(ethylmercapto)-propene-1 (IV).

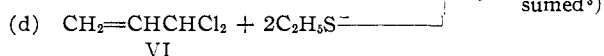
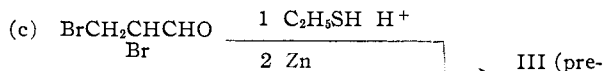


Rothstein assigned structure III to the compound

in question on the basis of the following evidence: (1) ozonolysis gave glyoxal (as the 2,4-dinitrophenylhydrazone), (2) reaction with mercuric chloride gave acrolein, (3) oxidation with hydrogen peroxide gave 1,3-(ethylsulfonyl)-propene-1 (V)⁴

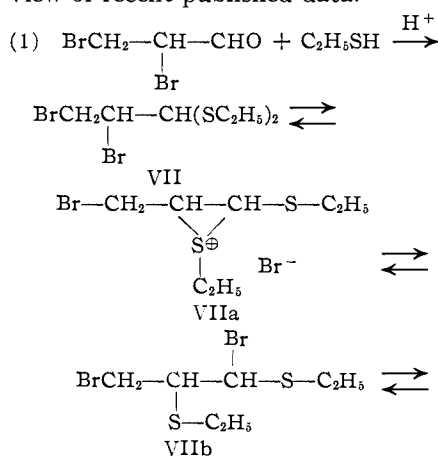


and (4) methods of preparation (equations c and d).



The failure of the compound in question to isomerize by reaction with alkali is inconsistent with structure III,⁵ but consistent with structure IV. The formation of glyoxalosazone from the ozonization mixture, described in 1, above, is consistent with either structure III or IV⁶; however, the absence of formaldehyde as a reaction product³ is consistent for only IV. The formation of acrolein by reaction of the compound in question with mercuric chloride is consistent with either structure III or IV. The first product expected by reaction of IV with mercuric chloride is β -ethylmercaptpropionaldehyde. We have shown that this aldehyde readily gives acrolein by reaction with aqueous mercuric chloride. Oxidation of the compound in question to V would appear to be consistent with structure IV, and inconsistent with structure III. Finally the infrared spectrum of the compound (prepared as shown in equation c) was shown to be consistent with that expected for IV, but not for III. Characteristic absorption of a terminal vinyl group III at 900 and 995 cm^{-1} was absent. The presence of conjugated unsaturation was indicated by a band at 1608 cm^{-1} and several bands between 900 and 1100 cm^{-1} .

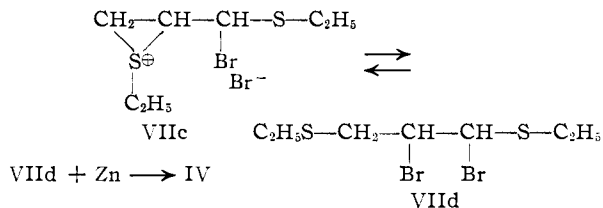
That the syntheses originally employed³ for the preparation of III (equations c and d) would lead instead to the formation of IV, is not unexpected in view of recent published data.



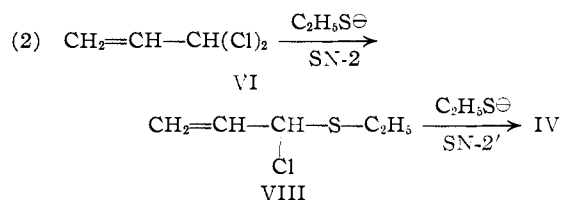
(4) E. Rothstein, *J. Chem. Soc.*, 1560 (1940). Rothstein suggested that molecular rearrangement occurred during the oxidation of III.

(5) D. S. Tarbell and M. A. McCall, *THIS JOURNAL*, **74**, 48 (1952).

(6) The product expected by ozonization of IV would be $\text{C}_2\text{H}_5\text{S}-\text{CH}_2\text{CHO}$. W. E. Parham and J. Jones, *THIS JOURNAL*, **76**, 1068 (1954), have shown that the reactions of α -alkylmercaptoacetaldehydes with phenylhydrazine or 2,4-dinitrophenylhydrazine give glyoxal osazones.

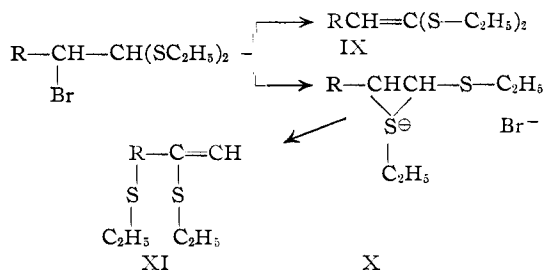


Rearrangements of β -halosulfides⁷⁻⁹ are well known, and it would be anticipated that VII could react as any of the forms VII-VIII.



de La Mare and Vernon¹⁰ have shown that VI undergoes nucleophilic attack by two mechanisms (SN2 and SN2'). Initial reaction of mercaptide ion with VI by an SN2 process, followed by a reaction of the first intermediate VIII with mercaptide ion by an SN2' process, would lead to IV.

The conclusion that IV is formed from dibromoacrolein, as shown in equation 1, casts considerable doubt upon the assignments of structure of many products previously derived from α -halomercaptals.^{3,11,12} Rothstein¹² and Whitely have pointed out the possible existence of sulfonium intermediates in the reactions of halomercaptals; however, their interpretations obviate the necessity of such intermediates. Specifically, it has been stated that α -halomercaptals spontaneously eliminate hydrogen halide to give ketenemercaptals^{11,12} (IX).



There appears to be no unequivocal evidence that ketene mercaptals result directly by the spontaneous elimination of hydrogen halide from α -halomercaptals. It is probable that such elimination reactions lead directly to the formation of 1,2-bis-(alkylmercapto)-ethylenes (XI) by molecular rearrangements involving sulfonium intermediates.

The relative stability of the contributing ions, X, Xa and Xb, would be expected to play an important role in determining the course of ϵ -1 reactions involving the halomercaptal. Products derived from Xb would be anticipated because: (1) the ion Xb

(7) R. C. Fuson, C. C. Price and D. Burness, *J. Org. Chem.*, **11**, 475 (1946).

(8) R. C. Fuson and A. J. Speziale, *THIS JOURNAL*, **71**, 1582 (1949).

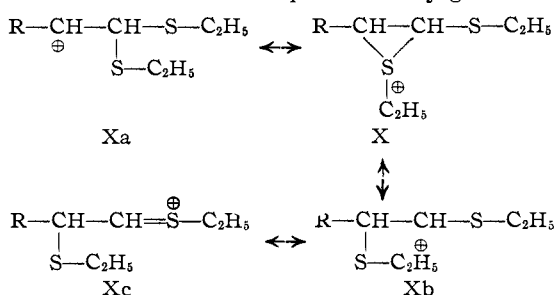
(9) C. S. Marvel and E. D. Weil, *ibid.*, **76**, 61 (1954).

(10) P. B. D. de La Mare and L. A. Vernon, *J. Chem. Soc.*, 3331 (1952).

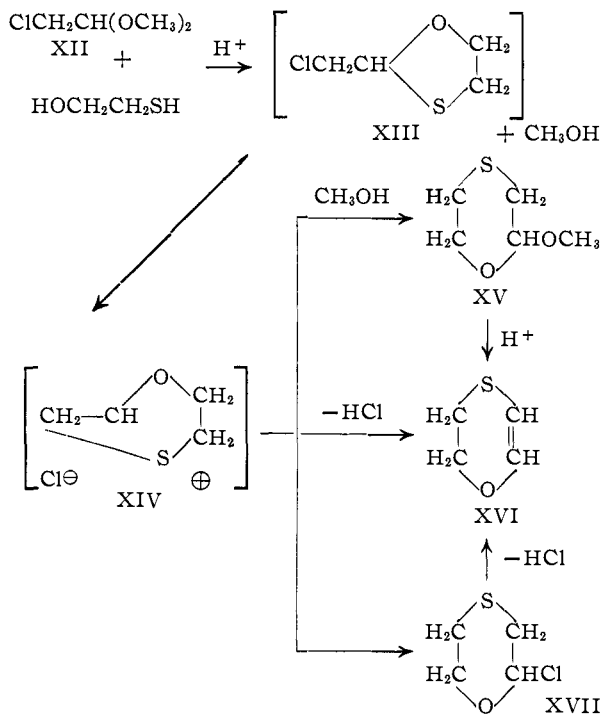
(11) E. Rothstein, *ibid.*, 1553 (1940).

(12) E. Rothstein and R. Whitely, *ibid.*, 4012 (1953).

would be stabilized by electron release from sulfur (Xc), and (2) the olefin derived from Xb (*i.e.*, XI) would have the maximum possible conjugation.¹³



A study of the reaction of haloacetals with difunctional mercaptans has been made: (1) as a proposed synthesis of heterocyclic vinyl sulfides, and (2) to obtain additional information concerning the course of the reactions of α -halomercaptals. When a mixture of chloroacetal (XII), monothioglycol and *p*-toluenesulfonic acid (catalyst) was heated to 80°, in the absence of solvent, a vigorous and somewhat uncontrolled reaction occurred. Methanol and hydrogen chloride were evolved.



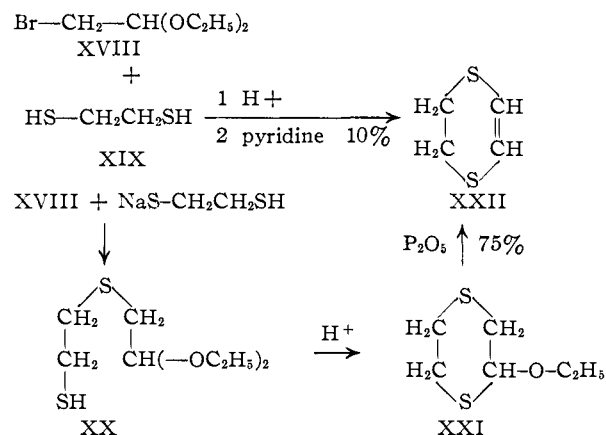
Distillation of the reaction mixture gave an oil (30% yield) which was composed principally of 2-methoxy-1,4'-oxathiane (XV). This product was identified by: (1) its boiling point and refractive index,¹⁴ (2) its composition (C and H), and (3) its conversion, in high yield, into the 2,4-dinitrophenylhydrazone of 2-hydroxyethylmercaptoacetaldehyde¹⁴ (m.p. and mixed m.p. 77–78°). The princi-

(13) Other products generally obtained by reaction of α -halomercaptals with mercaptans (*i.e.*, tris-sulfides) are consistent with this interpretation.¹² Derivatives^{3,11,12} of ketenemercaptals have been reported from such reactions; however, it is likely that these products are derived from the tris-sulfides or are incorrectly formulated.

(14) W. E. Parham, I. Gordon and J. Swalen, *THIS JOURNAL*, **72**, 913 (1950).

pal impurity was a chlorine-containing product which evolved hydrogen chloride during distillation to give 1,4-oxathiane (XVI).^{14,15} XVI was identified by: (1) its boiling point and refractive index,¹⁴ (2) its conversion into the 2,4-dinitrobenzenesulfonyl acetate derivative of 1,4-oxathiane (m.p. and mixed m.p. 148–149°),¹⁴ and (3) by its conversion into the 2,4-dinitrophenylhydrazone of 2-hydroxyethylmercaptoacetaldehyde by reaction with 2,4-dinitrophenylhydrazine. Loss of hydrogen chloride from the chlorine-containing product, and its conversion into XVI by distillation, suggested structure XVII for this material. Additional evidence for structure XVII was obtained by a study of the reaction of the chlorine-containing product with 2,4-dinitrophenylhydrazine. The corresponding hydrazone of 2-hydroxyethylmercaptoacetaldehyde was obtained. There was no evidence for the presence of the 2,4-dinitrophenylhydrazone of chloroacetaldehyde (the expected product from XIII). When the reaction of dimethyl chloroacetal and monothioglycol was carried out in carbon tetrachloride, an 18% yield of pure XV was obtained.¹⁶

The reaction of bromoacetal (XVIII), dithioglycol (XIX) and *p*-toluenesulfonic acid (catalyst) was carried out in benzene solution. The reaction product was treated with pyridine to effect removal of hydrogen bromide, and two products, a solid¹⁷ and a liquid, were obtained. The liquid product (10–23% yield) had the composition calculated for C₄H₆S₂, and was characterized by its conversion into the corresponding disulfone and monosulfilimine derivatives. The structure of the liquid



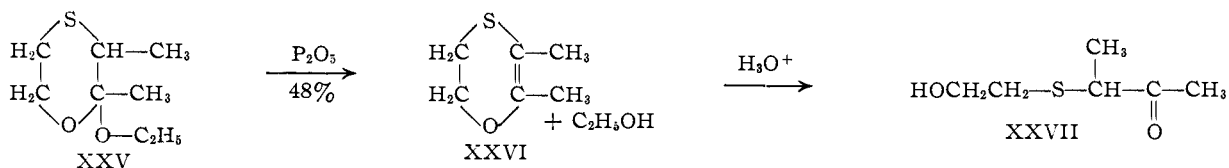
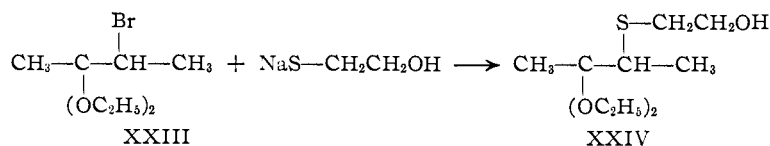
product was established as 1,4-dithiene (XXII), by its independent synthesis from XII as outlined in the above equations. The ultraviolet spectra of the two samples of XXII were identical, and mixtures of the corresponding monosulfilimine derivatives showed no depression in melting point. A 10% yield of 1,4-dithiene (XXII) was obtained when the reaction of diethyl bromoacetal and ethanedithiol was carried out in aqueous hydrochloric acid.

(15) 1,4-Oxathiane was also formed during the original reaction, or during the first distillation.

(16) A 17% yield of material which appeared to be impure XVI was also obtained; however, this product was not further investigated.

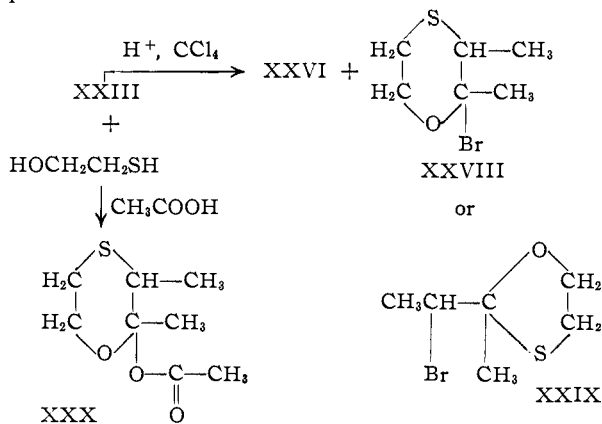
(17) The structure of the solid (m.p. 115–117°. 27% yield) is under investigation.

2,3-Dimethyl-1,4-oxathiene-2 (XXVI) was the expected product of the acid-catalyzed reaction of 2,2-diethoxy-3-bromobutane (XXIII) with monothioglycol (sulfonium mechanism). This unsaturated was first synthesized by the method summarized in the equations



The composition (C and H) of XXV, obtained by the intramolecular acetal interchange reaction of XXIV, indicated the product to be a mixture of XXV and XXVI. Loss of ethanol during the acid catalyzed cyclization of XXIV was not unexpected since the alkoxy group in XXV is tertiary. The mixture of XXV and XXVI was treated with phosphorus pentoxide to effect dealcoholization, and a 48% yield of XXVI was obtained. The product, XXVI, had the composition calculated for C₆H₁₀OS and readily gave biacetyl 2,4-dinitrophenylosazone, the expected product⁶ derived from XXVII, by reaction with 2,4-dinitrophenylhydrazine in acidic medium. The infrared spectrum of XXVI was consistent with the assigned structure.¹⁸

The reaction of 2,2-diethoxy-3-bromobutane (XXIII) with monothioglycol was first carried out with *p*-toluenesulfonic acid as the catalyst, in carbon tetrachloride solution. Two non-homogeneous products were obtained.



(18) The infrared spectrum of XXVI indicated a vinyl sulfide structure with no terminal double bond (absence of characteristic absorption at 900 and 995 cm.⁻¹). The spectrum possessed a band at 1662 cm.⁻¹, associated with a conjugated double bond, and bands at 700 and 2750 cm.⁻¹ (weak) which appear to be characteristic for cyclic vinyl sulfides (found also in the spectra of benzo-1,4-oxathiene,⁶ 1,4-oxathiene,¹⁴ and dihydrothiapyran). There was a band present at 1710 cm.⁻¹ which indicated a carbonyl impurity. When this band was strong (certain fractions of distillate) there appeared a band at 3400-3600 cm.⁻¹, indicating the presence of hydroxyl groups. Since vinyl ethers of type XVI and XXVI are known to hydrolyse easily,¹⁴ these absorptions have been attributed to the presence of small amounts of the expected hydrolysis product XXVII.

The first product (21.4% yield) contained no terminal vinyl groups (infrared spectrum) and was subsequently shown to be composed principally of 2,3-dimethyl-1,4-oxathiene-2 (XXVI). The boiling point and refractive index of this product were essentially identical to authentic XXVI, the infrared spectrum of the product showed only bands found in the spectrum of authentic XXVI,¹⁸ and finally, reaction of the product with 2,4-dinitrophenylhydrazine gave the correspond-

ing osazone of biacetyl—identical to that obtained from authentic XXVI.

The second product was assigned structure XXVIII on the basis of the following evidence: (1) analysis indicated the empirical formula C₆H₁₁OSBr, (2) reaction of the product with 2,4-dinitrophenylhydrazine gave the corresponding osazone of biacetyl,¹⁹ (3) reaction of the product with ethanolic silver nitrate gave an immediate precipitate of silver bromide—an observation commensurate with the α -haloether structure.

Two products were obtained when the reaction of XXIII and monothioglycol was effected using glacial acetic acid as the solvent. The physical properties of the lower boiling product suggested that XXVI was present; however, this material was not examined further. The higher boiling product (46%) was assigned structure XXX on the basis of its composition (C₈H₁₄SO₃), and by analogy to other reactions in this series.

The reactions described above are best explained by assuming cyclic sulfonium intermediates. It has been concluded that the loss of hydrogen halide from α -halomercaptals by the E-1 process is accompanied by molecular rearrangement, resulting in the formation of 1,2-bis-(alkylmercapto)-ethylenes. There is evidence²⁰ that the loss of hydrogen halide

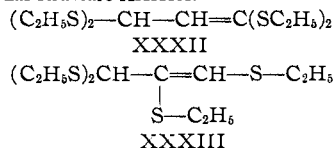
(19) This reaction would suggest that XXIX was not present to any considerable extent, for α -haloketones generally give hydrazones of α,β -unsaturated ketones in such reactions, and no such derivative was observed. Cf. F. Ramirez and A. F. Kirby, *THIS JOURNAL*, **74**, 433 (1952); *ibid.*, **75**, 6026 (1953).

(20) The loss of bromide from XXXI gives different products when

$$(\text{C}_2\text{H}_5\text{S})_2-\text{CH}-\underset{\text{Br}}{\text{CH}}-\text{CH}(\text{SC}_2\text{H}_5)_2$$

XXXI

pyridine and when potassium *t*-butoxide is used to effect the removal of hydrogen bromide. Rothstein¹² and Whitley have postulated that these products are geometric isomers of the ketenemercaptal XXXII; however, our work would suggest that one of the products (*i.e.*, that formed as a result of E-1 elimination of HBr, and presumably the product obtained by the use of pyridine) was formed by molecular rearrangement and thus has structure XXXIII.



from α -halomercaptals by the E-2 process does give ketenemercaptals; however, a different explanation prevails,²⁰ and additional experimental evidence is required to substantiate this latter hypothesis.

Experimental

The Reaction of Dimethyl Chloroacetal with Monothio-glycol without Solvent.—A mixture of dimethyl chloroacetal (60 g., 0.48 mole), monothioglycol (47.4 g., 0.48 mole) and *p*-toluenesulfonic acid (0.50 g.) was heated slowly to 80°. At this temperature a vigorous exothermic reaction occurred and some material (mostly hydrogen chloride and methanol) was lost through the condenser. The resulting mixture was cooled and solid potassium carbonate and water were added. The alkaline mixture was extracted with ether, and the ethereal extract was dried (magnesium sulfate-potassium carbonate) and distilled.

The first fraction (b.p. 66° (24 mm.), n_D^{25} 1.5135, 3.0 g.) was redistilled (b.p. 54° (22 mm.), n_D^{25} 1.5337) and was shown to consist principally of 1,4-oxanthiene (XVI).¹⁴ This material readily gave the 2,4-dinitrobenzenesulfonyl acetate derivative¹⁴ of XVI (m.p. and mixed m.p. 148–149°) by reaction with 2,4-dinitrobenzenesulfonyl chloride in acetic acid, and the 2,4-dinitrophenylhydrazone of 2-hydroxyethylmercaptoacetaldehyde¹⁴ (m.p. and mixed m.p. 77–78°) by reaction with 2,4-dinitrophenylhydrazine in acidic ethanol-water.

The second product (23.6 g., 37% yield, n_D^{25} 1.4960, b.p. 78–81° (24 mm.)) smelled of hydrogen chloride. This material was redistilled and was found to consist principally of 2-methoxy-1,4-oxathiane (XV, b.p. 85° (23 mm.), n_D^{25} 1.4931–1.4941; reported b.p.¹⁴ 71 (10 mm.), n_D^{25} 1.4911).

Anal. Calcd. for $C_6H_{10}O_2S$: C, 44.75; H, 7.51. Found: C, 44.85; H, 7.47.

An impurity, concentrated as a residue subsequent to the distillation of XV, contained chlorine and evolved hydrogen chloride upon attempted distillation giving XVI. Reaction of the chlorine-containing residue or XV with 2,4-dinitrophenylhydrazine in ethanol-water gave the 2,4-dinitrophenylhydrazone of 2-hydroxyethylmercaptoacetaldehyde (m.p. and mixed m.p. 77–78°¹⁴). There was no evidence for the formation of the 2,4-dinitrophenylhydrazone of chloroacetaldehyde which would have resulted if XIII had been present.

The Reaction of Dimethyl Chloroacetal with Monothio-glycol in Carbon Tetrachloride.—A solution of dimethyl chloroacetal (12.3 g., 0.1 mole), monothioglycol (7.85 g., 0.1 mole), *p*-toluenesulfonic acid (ca. 0.5 g.) and carbon tetrachloride (50 ml.) was heated slowly to the reflux temperature and then maintained at this temperature for 70 minutes. The reaction mixture (two phases) was cooled to room temperature and then washed with diluted sodium bicarbonate. The organic layer was dried (magnesium sulfate) and distilled. There was obtained 2.38 g. (18%) of 2-methoxy-1,4-oxathiane (XV, n_D^{25} 1.4911), identified as described above, and 2.31 g. (17%) of impure 1,4-oxathiene (XVI, b.p. 60° (5 mm.), n_D^{25} 1.5192–1.5208).

2-Ethoxy-1,4-dithiane (XXI).—The sodium salt of ethanedithiol was prepared by adding sodium (7.00 g., 0.304 gram atom) to ethanedithiol (28.77 g., 0.305 mole) in absolute ethanol (100 ml.). The entire reaction was conducted in an atmosphere of nitrogen. Diethyl bromoacetal (60 g., 0.305 mole) was then added and the resulting mixture was allowed to stand for 12 hours. Water (600 ml.) was added to the reaction mixture and then the pH of the resulting mixture was adjusted to 7.8 by carbonation with carbon dioxide. The oil which separated, was extracted with ether, dried (magnesium sulfate), and distilled. When the temperature of the liquid reached 130° (5 mm.), foaming occurred and ethanol was eliminated.²¹ The distillation was continued and two main fractions were obtained: (1)

10 g. (25% yield), b.p. 101–110° (10 mm.), n_D^{25} 1.53; (2) 6.3 g. (10% yield),²¹ b.p. 110–183–186° (10 mm.), n_D^{25} 1.51. Pure XXI (b.p. 88° (5 mm.), n_D^{25} 1.5410, 8.1 g.) was obtained by redistillation of fraction 1.

Anal. Calcd. for $C_6H_{12}OS_2$: C, 43.86; H, 7.37. Found: C, 43.79; H, 7.29.

1,4-Dithiene (XXII).—The procedure used was essentially that previously described¹⁴ for the dealcoholization of 2-ethoxy-1,4-oxathiane. At 145–175°, a 7.0-g. (0.043 mole) sample of 2-ethoxy-1,4-dithiane lost 1.5 g. (76%) of ethyl alcohol in 65 minutes. Distillation of the residue gave 3.8 g. (75%) of XXII as a faintly straw colored mobile oil (b.p. 101° (29 mm.), n_D^{25} 1.6295, λ_{max}^{282} (log ϵ 3.64), λ_{min}^{263} (log ϵ = 3.22)).

Anal. Calcd. for $C_4H_4S_2$: C, 40.64; H, 5.12. Found: C, 40.65; H, 5.37.

The tetroxide of XXII was prepared by reaction with hydrogen peroxide in acetic acid. The product was crystallized from acetic acid (decomposed between 200–300° with no sharp melting point).

Anal. Calcd. for $C_4H_4S_2O_4$: C, 26.37; H, 3.32. Found: C, 26.64; H, 3.33.

The monosulfilimine derivative of XXII was prepared in aqueous methanol and recrystallized from ethanol; m.p. 128.5–129°.

Anal. Calcd. for $C_{11}H_{13}S_3O_2N$: C, 45.97; H, 4.56. Found: C, 46.04; H, 4.83.

The Reaction of Diethyl Bromoacetal with Ethanedithiol in Benzene.—A mixture containing ethanedithiol (4.7 g.), 0.05 mole, bromoacetal (9.85 g., 0.05 mole), benzene (30 ml.) and *p*-toluenesulfonic acid (ca. 0.05 g.) was heated at the reflux temperature for two hours. The oil (4.85 g.) that separated was removed, and the benzene solution was treated with 5 ml. of pyridine and warmed on a steam-bath for 30 minutes. The pyridine hydrobromide that formed was removed, and the benzene solution was washed with dilute hydrochloric acid and water. The benzene solution was dried (K_2CO_3), and the solvent was removed by distillation at reduced pressure. Ether was added to the residue, and 2.86 g. of a solid (m.p. 110–114°, 27%) was collected. The solid melted at 115–117° after recrystallization from acetone.

Anal. Calcd. for $C_{10}H_{16}S_2$: C, 36.33; H, 5.48. Found: C, 36.12; H, 5.51.

The ether solution was distilled and 1.35 g. (23%) of impure 1,4-dithiene (b.p. 88° (20 mm.), n_D^{25} 1.61) was obtained. The combined product of several experiments was redistilled to give pure 1,4-dithiene (n_D^{25} 1.6273, m.p. and mixed m.p. of the monosulfilimine derivative 128–129°). The ultraviolet spectrum of this material was identical to authentic XXII.

The Reaction of Diethyl Bromoacetal and Ethanedithiol in Aqueous Hydrochloric Acid.—A mixture of ethanedithiol (9.4 g., 0.1 mole), bromoacetal (19.2 g., 0.1 mole), water (250 ml.) and concentrated hydrochloric acid (0.5 ml.) was allowed to stand for 24 hours, and was then heated at the reflux temperature for one hour. The water-insoluble oil was extracted with ether, dried and distilled to give 1.1 g. of 1,4-dithiene (spectrum identical to authentic XXII, b.p. 75° (15 mm.), n_D^{25} 1.6296, m.p. and mixed m.p. of the monosulfilimine derivative was 128–129°).

3-Bromo-2-butanone, b.p. 48–49° (7 mm.), was prepared in 51% yield from 2-acetoxy-2-butene^{22,23} by the method of Bedoukian.²³

2,2-Diethoxy-3-bromobutane (XXIII) was prepared in 39.5% yield from 3-bromo-2-butanone by a procedure essentially identical to that previously described for the corresponding chloro derivative²⁴; b.p. 44–45° (1.4 mm.), n_D^{20} 1.4420.

Anal. Calcd. for $C_8H_{17}O_2Br$: C, 42.68; H, 7.61. Found: C, 42.29; H, 7.82.

A sample of XXIII (2.03 g.) was hydrolyzed with barium carbonate (2.0 g.) in water by a procedure similar to that described for the hydrolysis of 3-bromo-2-butanone.²⁵ The

(21) In this experiment an attempt was made to isolate the intermediate 2-mercaptoethylmercaptoacetaldehyde diethyl acetal; however, this compound partly cyclized upon distillation. For the preparation of 2-ethoxy-1,4-dithiane it is recommended that the 2-mercaptoethylmercaptoacetaldehyde diethyl acetal be cyclized by the action of mineral acid, by a procedure similar to that previously described for the cyclization of 2-hydroxyethylmercaptoacetaldehyde diethyl acetal (cf. ref. 14).

(22) W. M. Quattlebaum and C. A. Noffsinger, British Patent 615,521; C. A., 43, 7953 (1949).

(23) P. Z. Bedoukian, THIS JOURNAL, 67, 1430 (1945).

(24) A. Youtz and P. P. Perkins, *ibid.*, 51, 3513 (1929).

(25) A. Favorskii and B. Issachenko, *J. prakt. Chem.*, 88, 656 (1913).

resulting mixture was treated with phenylhydrazine hydrochloride and was heated at the reflux temperature for 45 minutes. The solid that separated was identified as biacetylosazone (m.p. and mixed m.p. 243–249.5°).

2,3-Dimethyl-1,4-oxathiene-2 (XXVI).²⁶—Monothioglycol (7.81 g., 0.1 mole) was added to a solution prepared from sodium (2.30 g., 0.1 g. atom) and absolute ethanol (50 ml.). 2,2-Diethoxy-3-bromobutane (22.5 g., 0.1 mole) was added, and the resulting mixture was allowed to stand at room temperature for 24 hours. The reaction mixture was protected from moisture during the entire period. The sodium bromide that precipitated was removed and the ethanol was distilled at reduced pressure. Dry ether (100 ml.) was added to the residue and the solution was made acidic with a few drops of concentrated sulfuric acid. The resulting mixture was allowed to stand at room temperature for 12 hours. The solution was neutralized with solid sodium carbonate, filtered and distilled. Analysis of the product (7.37 g., ca. 42% yield, b.p. 87–89° (15 mm.), n_D^{25} 1.5170) indicated it to be a mixture of 2-ethoxy-2,3-dimethyl-1,4-oxathiane (XXV) and 2,3-dimethyl-1,4-oxathiene-2 (XXVI).

Anal. Calcd. for $C_8H_{16}O_2S$: C, 54.51; H, 9.15. Calcd. for $C_8H_{10}OS$: C, 55.34; H, 7.74. Found: C, 54.63; H, 7.83.

A sample (4.93 g.) of the product, described above, was placed in a small distilling flask and phosphorus pentoxide (0.10 g.) was added. The flask was immersed in an oil-bath, and was slowly heated to 174° and held at that temperature until ebullition ceased. The reaction mixture was then cooled, more phosphorus pentoxide was added (ca. 0.1 g.), and the resulting mixture was distilled at reduced pressure, affording 1.75 g. (48%) of XXVI (b.p. 59–63° (21 mm.), n_D^{25} 1.5187). The material was redistilled (b.p. 68° (22 mm.), n_D^{25} 1.5183) for analysis.

Anal. Calcd. for $C_8H_{10}OS$: C, 55.34; H, 7.74. Found: C, 55.17; H, 8.11.

The reaction of XXV with 2,4-dinitrophenylhydrazine in phosphoric acid-ethanol resulted in the formation of biacetyl-2,4-dinitrophenylosazone (m.p. and mixed m.p. 315° dec.).

The Reaction of 2,3-Diethoxy-3-bromobutane (XXIII) with Monothioglycol in Carbon Tetrachloride.—A solution of monothioglycol (6.46 g., 0.055 mole) in carbon tetrachloride (5 ml.) was added to a cold (0°) solution prepared from XXIII (12.49 g., 0.055 mole), *p*-toluenesulfonic acid (5 mg.) and carbon tetrachloride (25 ml.). The resulting solution was allowed to come to room temperature. Gas evolution resulted, and the reaction mixture separated into two phases. The mixture was allowed to stand at room temperature for three days, then diluted with chloroform, washed with 5% sodium carbonate, dried (magnesium sulfate), and distilled. Two principal fractions were obtained: (1) 2.10 g. (29%), b.p. 84° (20 mm.), n_D^{25} 1.5198, and (2) 2.70 g. (23%), b.p. (2.3 mm.), n_D^{25} 1.5258.

Fraction 1 was shown to be composed principally of 2,3-dimethyl-1,4-oxathiene-2 (XXVI). The material was redistilled (n_D^{25} 1.5188–1.5211) and the infrared spectra of various fractions compared to authentic 2,3-dimethyl-1,4-methyl-1,4-oxathiene-2. The spectra were essentially identical to authentic XXVI and showed no terminal unsaturation. The product reacted readily with 2,4-dinitrophenylhydrazine (phosphoric acid-water-ethanol) to give bi-

(26) This procedure was patterned after that previously described (see reference 14) for the preparation of 1,4-oxathiene (XVI).

acetyl-2,4-dinitrophenylosazone (m.p. and mixed m.p. 315° dec.).

Fraction 2 was composed of material to which structure XXVIII has been assigned. A sample with n_D^{25} 1.5244 was used for analysis.

*Anal.*²⁷ Calcd. for $C_8H_{11}OSBr$: C, 34.13; H, 5.25; Br, 37.85. Found: C, 34.25; H, 5.66; Br, 36.79.

Reaction of XXVIII with 2,4-dinitrophenylhydrazine (phosphoric acid method) afforded biacetyl-2,4-dinitrophenylosazone (m.p. and mixed m.p. 314° dec.).

The Reaction of 2,2-Diethoxy-3-bromobutane (XXIII) with Monothioglycol in Acetic Acid Solution.—Monothioglycol (4.4 g., 0.0526 mole) was added slowly to an ice-cold, well-stirred solution prepared from XXIII (11.82 g., 0.0526 mole), *p*-toluenesulfonic acid (5 mg.) and glacial acetic acid (26 ml.). The cold mixture was stirred for six hours, then diluted with water and extracted with ether. The ethereal extract was washed with 5% aqueous sodium bicarbonate, dried over magnesium sulfate, and distilled. The principal product, 4.51 g. (46% yield), b.p. 83–84° (1 mm.), n_D^{25} 1.4758, has been assigned structure XXX.

Anal. Calcd. for $C_8H_{14}O_3S$: C, 50.50; H, 7.42. Found: C, 50.30; H, 7.29.

This material also gave biacetyl-2,4-dinitrophenylosazone upon reaction with acidic 2,4-dinitrophenylhydrazine—the osazone was purified by chromatography on silica-gel using petroleum ether-benzene (2:1) as eluant.

1,3-Bis-(ethylmercapto)-propene-1 (IV).—This product was prepared from 2,3-dibromopropionaldehyde and ethyl mercaptan by a procedure previously described.³ The product (b.p. 70° (1 mm.), n_D^{25} 1.5315) had previously been considered to be acrolein diethyl mercaptal (III). The infrared spectrum of the product showed the absence of a terminal vinyl group. A summary of the spectrum is found in the text of this report.

3-Ethylmercaptopropionaldehyde.—Ethyl mercaptan (7.53 g., 0.150 mole) was added to a solution prepared from sodium (2.80 g., 0.122 g. atom) and absolute ethanol (40 ml.), and 3-chloropropionaldehyde diethyl acetal²⁸ was added. The mixture was heated at the reflux temperature for two hours, then cooled, acidified (dilute hydrochloric acid), and the acid solution was allowed to stand for several hours to effect hydrolysis of the acetal linkage. The crude aldehyde was extracted with ether and the ethereal extract was dried (magnesium sulfate) and distilled. 3-Ethylmercaptopropionaldehyde (7.91 g.) was collected at 58–63° (11 mm.) (reported⁴ b.p. 60° (10 mm.)).

The Reaction of 3-Ethylmercaptopropionaldehyde with Mercuric Chloride.—A solution of mercuric chloride (9.10 g., 33.4 mmoles) in water (28 ml.) was heated on a steam-bath, and 3-ethylmercaptopropionaldehyde (7.91 g., 66.8 mmoles) was added. A white solid precipitated and material distilled (b.p. 52–80°) from the reaction mixture. The distillate was shown to contain appreciable quantities of acrolein by its conversion into acrolein 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. 161–163°).

MINNEAPOLIS MINN.

(27) The bromine in this product was quite active and readily precipitated silver bromide from a solution of silver nitrate in ethanol. The bromine analysis was semiquantitative.

(28) E. J. Witzemann, W. L. Evans, H. Hass and E. F. Schroeder, "Organic Syntheses," Col. Vol. 11, J. Wiley and Sons, New York, N. Y., 1948, p. 137.