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BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Cyclic Sulfones. VI. Synthesis and Reactions of 4-Hydroxythiaepane 1,1-Dioxide[1]

BY C. G. OVERBERGER AND A. KATCHMAN[2]

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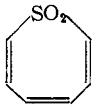
Reaction of tetrahydro-1,4-thiapyrone with diazomethane gave a 42% yield of 4-ketothiaepane (VIII) and a 40% yield of the oxide IX. Reaction of tetrahydro-1,4-thiapyrone 1,1-dioxide with diazomethane gave only the oxide, V, and none of the seven-membered ring. Treatment of 4-aminomethyltetrahydrothiapyran 1,1-dioxide-4-ol (IVa) with nitrous acid gave 4-oxothiaepane 1,1-dioxide (VI) in low yield and V in 67% yield. VIII was converted to the corresponding carbinol and then oxidized and acetylated to give 4-acetoxythiaepane 1,1-dioxide (XIII). Other reactions of this acetate are also described.

The synthesis of thiaepin or thiaepin 1,1-dioxide (I) is of interest because it represents a case in which the concept that (2 + 4 *N*) or 6π-electrons are necessary for aromatic resonance,[3] can be examined for a sulfur system, although planarity is unlikely. A knowledge of the degree of aromatic character of this compound would be of considerable theoretical interest. This paper reports the preparation of key intermediates for the synthesis of thiaepin and thiaepin 1,1-dioxide.

The proposed synthesis of thiaepin 1,1-dioxide used tetrahydro-1,4-thiapyrone 1,1-dioxide[4] (II) as the starting material. An initial attempt at ring enlargement using the procedure described by Kohler, *et al.*,[5] with diazomethane resulted in the isolation of a small amount of the oxide V and none of the desired 4-ketothiaepane 1,1-dioxide (VI). An alternate route for ring enlargement was the method of Tiffeneau, *et al.*,[6] which required as the key step the diazotization of 4-aminomethyltetrahydrothiapyran 1,1-dioxide-4-ol (IVa). The compound was conveniently prepared by the condensation of nitromethane with the keto sulfone II with sodium ethoxide to give 4-nitromethyltetrahydrothiapyran 1,1-dioxide-4-ol (III) in 71% yield. Catalytic reduction of the nitro alcohol in methanol with hydrogen at 3 atmospheres gave the amino alcohol IVa in 88% yield while a similar reduction in acetic acid gave the acetate salt IVb in an 86% yield. Diazotization of IVb in 10% glacial acetic acid gave as the major product the oxide V in a 67% yield, characterized as the glycol, while 4-ketothiaepane 1,1-dioxide (VI) was obtained as a side product in a 13.6% yield. Attempts to alter the course of the reaction by increasing the acidity of the solvent, for example, the use of 20, 40% glacial acetic acid and 50% sulfuric acid failed. An attempt to prepare 4-nitromethyltetrahydrothiapyran-4-ol by a condensation of VII with nitromethane with sodium ethoxide gave the sodium salt of the nitro alcohol which on acidification gave only starting material.



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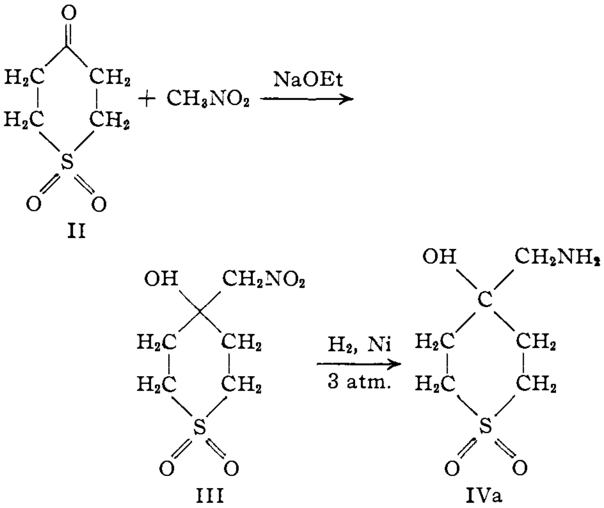

II

III

IVa

Repetition of the diazomethane type ring enlargement on tetrahydro-1,4-thiapyrone[4] using barium oxide[7] as the basic catalyst for the decomposition of nitrosomethylurethan proved successful. There was obtained as a colorless liquid 4-ketothiaepane (VIII) in a 42% yield, characterized by the formation of its 2,4-dinitrophenylhydrazone. The

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[1] This is the sixth in a series of papers concerned with cyclic sulfones. For the previous paper in this series, see C. G. Overberger, R. A. Gadea, J. A. Smith and I. C. Kogon, THIS JOURNAL, **75**, 2075 (1953).

[2] This paper comprises part of a thesis presented by Arthur Katchman in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the graduate school of the Polytechnic Institute of Brooklyn.

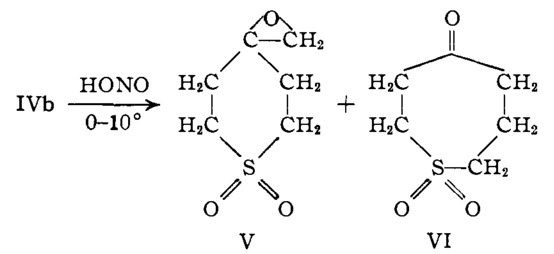
[3] E. Hückel, *Z. Elektrochem.*, **43**, 752 (1937).

[4] E. A. Fehnel and M. Carmack, THIS JOURNAL, **70**, 1813 (1948).

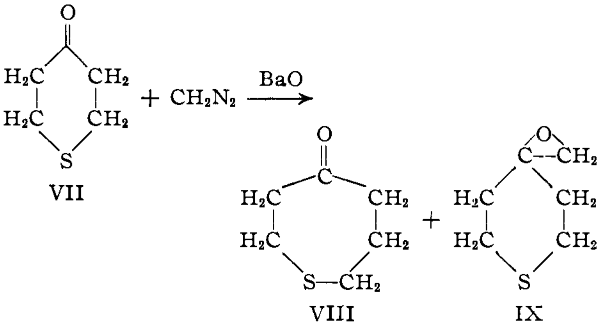
[5] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *ibid.*, **61**, 1057 (1939).

[6] M. Tiffeneau, E. Weill and B. Tchoubar, *Compt. rend.*, **205**, 54 (1937).

[7] The use of barium oxide in the ring expansion of the sulfide was suggested by Dr. H. J. Dauben, Univ. of Washington, Seattle. There are a number of indications that electron withdrawing groups favor the oxide in the reaction of diazomethane with ketones although steric factors may also be operative. Thus cyclohexanone gives a ketone:oxide ratio of *ca.* 4 (Kohler, *et al.*, THIS JOURNAL, **61**, 1057 (1939)); 2-chlorocyclohexanone gives a ketone:oxide ratio of no greater than about 1:1 and probably much less [D. Gutsche, *ibid.*, **71**, 3513 (1949) and unpublished observations]. In work presented by Dr. Gutsche last summer the ketone:oxide ratio was measured for a number of ketones of the general type 2-(*p*-R-phenyl)-cyclohexanone and was found to be 3.45 when R is hydrogen, 5.45 when R is methoxyl and 2.65 when R is chloro. It would seem therefore that electron withdrawing substituents which have strong inductive effects on the carbonyl dipole do favor oxide formation.



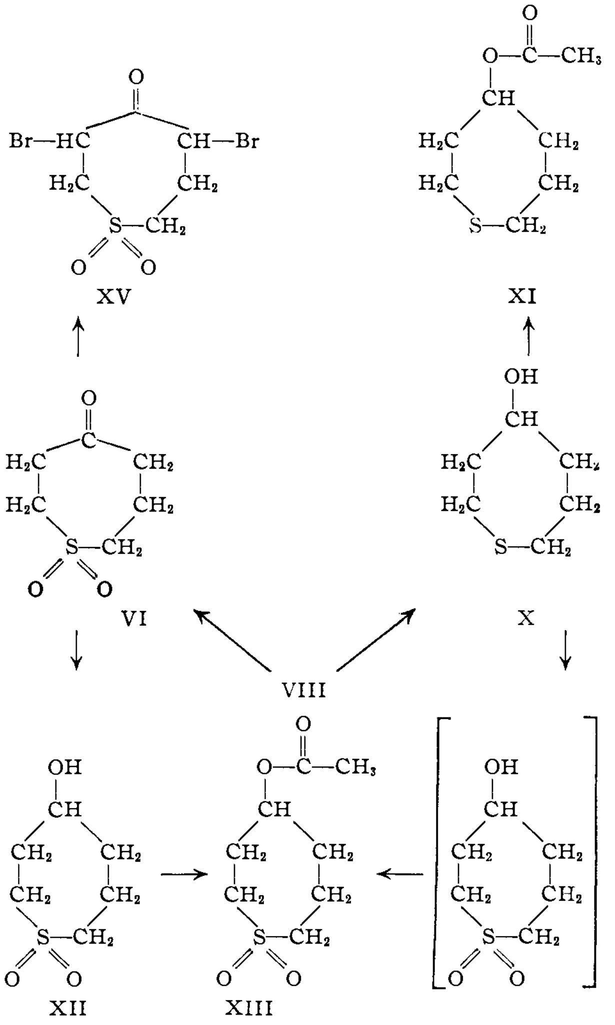
infrared spectrum showed strong carbonyl absorption at 1710 cm.$^{-1}$ while the oxide IX which was obtained as solid, m.p. 50–52°, in 40% yield showed no carbonyl absorption. Reduction of 4-ketothiaepane (VIII) was accomplished smoothly by both lithium aluminum hydride in 90% yield and aluminum isopropoxide in 71% yield. The carbinol, 4-hydroxythiaepane (X), was obtained as a colorless liquid which was characterized as the acetate, 4-acetoxythiaepane (XI).



4-Acetoxythiaepane 1,1-dioxide (XIII) was obtained by the oxidation of 4-hydroxythiaepane (X) in glacial acetic acid with 30% hydrogen peroxide. No attempt was made to isolate the intermediate 4-hydroxythiaepane 1,1-dioxide since this was partially acetylated in the oxidation step. The crude oxidation product was refluxed with acetyl chloride to give the acetate sulfone XIII in an over-all 95% yield.

An alternate but more difficult route to 4-acetoxythiaepane 1,1-dioxide (XIII) was the oxidation of 4-ketothiaepane (VIII) in formic acid with 30% hydrogen peroxide to give 4-ketothiaepane 1,1-dioxide (VI) in 77.5% yield. Catalytic reduction with Raney nickel at 100 atmospheres and 100° gave 4-hydroxythiaepane 1,1-dioxide (XII), which on acetylation with acetyl chloride gave XIII.

An attempt to pyrolyze XIII through a packed tube heated over temperatures ranging from 300–500° gave poor results. The deacetylation was accomplished simply and in excellent yield by refluxing the acetate at its boiling point until all of the acetic acid had distilled. From this reaction there was obtained a crystalline solid, which is a monoolefin and which probably is a mixture of Δ^3- and Δ^4-tetrahydrothiaepin 1,1-dioxides (XIV). Attempts to isomerize the mixture thermally and with acid or base failed. Attempts to separate the isomers chromatographically and by crystallization also failed. If the deacetylation was carried out under milder conditions, a higher melting monoolefin, 107–112°, was obtained by repeated recrystallizations from ethanol in the cold. Attempted dehydrogenation of the olefin mixture with selenium dioxide resulted in a very small yield of monoolefin, m.p. 114–115°. Attempted peroxidation with peracetic acid also gave a small amount of the same monoölefin. Reaction of this olefin with N-bromosuccinimide in the presence of benzoyl peroxide gave an allylic monobromide, analytically pure, m.p. 92–93°. Further work is in progress on these reactions.



Bromination of VI gave XV in 90% yield. The addition of bromine to a mixture of tetrahydrothiaepin 1,1-dioxides (XIV) proceeded rapidly and exothermically, resulting in a mixture of dibromothiaepane 1,1-dioxides (XVI). Repeated recrystallization of the mixture gave a small amount of dibromothiaepane 1,1-dioxide, m.p. 132–134°. The higher melting material undoubtedly was a purified sample of one of the isomers. A low melting product also was obtained which was apparently a mixture of isomers.

Dehydrohalogenation of the dibromide mixture gave a vinyl bromide. Reaction of the dibromide mixture with dimethylamine gave a monobromodimethylamino derivative. Since the exact structure of these products was not determined, a structural formula has not been proposed.

Experimental[8]

4-Nitromethyltetrahydrothiapyran 1,1-Dioxide-4-ol (III).—A condensation procedure adapted from that of Grob and von Tscharner,[9] was used. To a solution of 2.3 g. (0.1 g. atom) of sodium in 150 ml. of absolute ethanol was added dropwise a hot solution consisting of 70 ml. of absolute ethanol, 30 ml. of nitromethane and 14.8 g. (0.1 mole) of tetrahydro-1,4-thiapyrone 1,1-dioxide (II).[4] The sodium salt of the nitro alcohol separated immediately as a white precipitate. After the addition was complete, the mixture was stirred for 2 or 3 hours and then allowed to stand overnight at room temperature. The precipitate was removed by filtration and the remaining filtrate was removed under reduced pressure to obtain more salt. The combined salt was dissolved in ice-water and neutralized with acetic acid which immediately precipitated the nitro alcohol from solution, 14.8 g. (71%), m.p. 156–158°. Recrystallization from methanol raised the melting point to 158–159.5°.

Anal. Calcd. for $C_6H_{11}NO_5S$: C, 34.44; H, 5.30; N, 6.70; S, 15.32. Found: C, 34.44; H, 5.40; N, 6.83; S, 15.12.

4-Aminomethyltetrahydrothiapyran 1,1-Dioxide-4-ol (IVa) and its Acetate IVb. (A).—A mixture of 20.9 g. (0.1 mole) of nitro alcohol III, 150 ml. of methanol and *ca.* 1.0 g. of Raney nickel W_2 catalyst[10] was shaken under hydrogen overnight in a Parr apparatus at 3 atmospheres. The theoretical uptake of hydrogen was observed for reduction of a nitro group. The catalyst was removed by filtration and the solvent removed under reduced pressure, 15.8 g. (88.2%) m.p. 173–175°, of white crystalline material. Sublimation gave an analytical sample melting at 179–180°.

Anal. Calcd. for $C_6H_{13}NO_3S$: C, 40.21; H, 7.31; N, 7.82; S, 17.89. Found: C, 40.28; H, 7.24; N, 7.93; S, 17.72.

(B) The acetic acid salt IVb was obtained when glacial acetic acid was used as the solvent for the reduction of III. A mixture of 20.9 g. (0.1 mole) of nitro alcohol II, 150 ml. of glacial acetic acid and *ca.* 1.0 g. of Raney nickel W_2 catalyst gave a green viscous oil after removal of catalyst and solvent. The oil was triturated with ether and placed in the cold overnight, solidification with crystallization taking place. Filtration of the solid gave 20.6 g. (86.2%), m.p. 169–171°, of the acetic acid salt of 4-aminomethyltetrahydrothiapyran 1,1-dioxide-4-ol. Recrystallization from methanol at low temperatures raised the melting point to 175–176.5°.

Anal. Calcd. for $C_8H_{17}NO_5S$: C, 40.11; H, 7.13; S, 13.39. Found: C, 40.00; H, 7.23; S, 13.21.

4-Hydroxymethyltetrahydrothiapyran 1,1-Dioxide-4-ol.—Hydrolysis was effected by refluxing 1.2 g. (0.0074 mole) of the epoxide V in 50 ml. of a 20% solution of sulfuric acid for 3 or 4 hours. The cooled solution was diluted with 100 ml. of ice-water and neutralized with barium hydroxide. The precipitated barium sulfate was removed by filtration and the filtrate evaporated to dryness under reduced pressure. The solid residue was recrystallized from methanol to give 0.95 g. (71.3%), m.p. 162–164°, of the crystalline glycol. Recrystallization from methanol raised the melting point to 163–164.5°.

Anal. Calcd. for $C_6H_{12}O_4S$: C, 39.98; H, 6.71; S, 17.79. Found: C, 39.85; H, 6.59; S, 17.69.

Diazotization of the Amine Acetate IVb. Preparation of Oxide V.—The procedure was essentially that employed for usual diazotization reactions. To a solution of 47.8 g. (0.2 mole) of the amine acetate IVb dissolved in 250 ml. of a 10% solution of glacial acetic acid maintained at 0–10° was added dropwise a 40% solution of sodium nitrite. During the addition the oxide separates out and upon completion the mixture was stirred for 2 hours. The cold solution was filtered giving 21.7 g. (67%) of white crystalline material, m.p. 169–171°. Sublimation gave an analytical sample melting at 173–174°.

Anal. Calcd. for $C_6H_{10}O_3S$: C, 44.43; H, 6.22; S, 19.77. Found: C, 44.49; H, 6.20; S, 19.78.

The infrared spectrum indicated no carbonyl absorption in the region of 1650–1750 cm.$^{-1}$.

The Reaction of Tetrahydro-1,4-thiapyrone with Diazomethane: Preparation of 4-Oxothiaepane (VIII) and the Oxide IX.—The procedure used for the ring enlargement was a modification of the one described by Kohler, *et al.*,[5] for ring enlargement of cyclohexanone. To a solution of 116 g. (1.0 mole) of tetrahydro-1,4-thiapyrone in 250 ml. of methanol, which was made slightly alkaline by the addition of barium oxide, was added 133 g. (1.0 mole) of nitrosomethylurethan.[11] During the course of the addition, 2–3 g. of barium oxide was added in small portions and upon completion the mixture was allowed to stir for 1 hour. The mixture was filtered and the solvent removed under reduced pressure. The residual oil was diluted with a large amount of ether to precipitate out the polymethylene polymers, filtered, the ether removed and the residue fractionated through a column packed with glass helices. Distillation gave two major fractions: (1) a colorless liquid, 44.5 g., b.p. 58–63° (1.5 mm.), which crystallized immediately in the receiver, m.p. 50–52°, and was identified as the oxide IX; and (2) a colorless liquid, b.p. 72–75° (1.5 mm.), 46.8 g., $n^{23}D$ 1.5299, d^{20}_4 1.1351, which was identified as 4-oxothiaepane (VIII). The intermediate fraction, b.p. 63–72° (1.5 mm.), consisted of a mixture of oxide and ketone which on distillation gave an additional 7.5 g. of oxide and 8.0 g. of ketone. The combined yield of oxide obtained was 52.0 g. (40%) and of ketone, 54.8 g. (42%).

Anal. Calcd. for $C_6H_{10}OS$ (IX): C, 55.35; H, 7.74; S, 24.62. Found: C, 55.22; H, 7.62; S, 24.27.

The infrared spectrum indicated no carbonyl absorption in the region 1650–1750 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{10}OS$ (VIII): C, 55.35; H, 7.74; S, 24.62. Found: C, 55.49; H, 7.87; S, 24.23.

The infrared spectrum showed strong carbonyl absorption at 1710 cm.$^{-1}$.

A 2,4-dinitrophenylhydrazone was prepared according to the method of Shriner and Fuson[12]; recrystallization from 95% ethanol gave a m.p. 189.5–191°.

Anal. Calcd. for $C_{12}H_{14}N_4O_4S$: C, 46.44; H, 4.56. Found: C, 46.61; H, 4.70.

4-Hydroxythiaepane (X). (A) **Aluminum Isopropoxide.** (B) **Lithium Aluminum Hydride.** (A).—A procedure similar to that described by Wilds[13] was used for the reduction of the ketone VIII. To a solution of 10.0 g. (0.049 mole) of freshly distilled aluminum isopropoxide in 150 ml. of isopropyl alcohol was added 10.0 g. (0.077 mole) of 4-oxothiaepane. The mixture was allowed to reflux for 1 hour and then distilled at such a rate that in 6 hours there remained 40–50 ml. of solution in the flask. The cooled reaction mixture was acidified with dilute hydrochloric acid and extracted with methylene chloride. The methylene chloride was dried over anhydrous sodium sulfate, the solvent removed by distillation and the residual oil distilled through a Vigreux column giving 7.3 g. (71.3%) of a colorless liquid, b.p. 75–77° (1 mm.), $n^{24}D$ 1.5379, d^{20}_4 1.1306.

Anal. Calcd. for $C_6H_{12}OS$: C, 54.50; H, 9.15; S, 24.25. Found: C, 54.48; H, 9.16; S, 24.31.

The infrared spectrum showed strong hydroxyl absorption at 3100 cm.$^{-1}$.

(B).—A procedure similar to that described by Brown[14] was used for the reduction. To a solution of 6.0 g. (0.16 mole) of lithium aluminum hydride in 300 ml. of absolute ethyl ether was added dropwise a solution of 50.0 g. (0.384 mole) of 4-oxothiaepane in 100 ml. of absolute ethyl ether. After completion of the addition the mixture was allowed to stir for 1 hour and then decomposed with water. The ether was removed by distillation and the residual oil was distilled through a Vigreux column giving 46.0 g. (90%), b.p. 78–80° (1.25 mm.), $n^{24}D$ 1.5379, d^{20}_4 1.1305.

4-Acetoxythiaepane (XI).—This compound was obtained as a colorless oil, b.p. 80–82° (2.1 mm.), $n^{25}D$ 1.4998, on

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[8] Microanalyses by Drs. Weiler and Strauss, Oxford, England, and Dr. K. Ritter, Zurich, Switzerland. All melting points are corrected.

[9] C. A. Grob and W. v. Tscharner, *Helv. Chim. Acta*, **33**, 1070 (1950).

[10] R. Mozingo, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 181.

[11] W. W. Hartman and R. Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 464.

[12] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., p. 171.

[13] A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 178.

[14] W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., p. 469.

treatment of the carbinol X with excess acetyl chloride under reflux (91%).

Anal. Calcd. for $C_8H_{14}O_2S$: C, 55.14; H, 8.10. Found: C, 55.39; H, 8.35.

4-Oxothiaepane 1,1-Dioxide (VI). (A).—To a solution of 10.0 g. (0.077 mole) of 4-oxothiaepane (VIII) in 75 ml. of formic acid was added 20 ml. (0.175 mole) of 30% hydrogen peroxide in small portions while the mixture was cooled intermittently in an ice-bath to moderate the reaction. After the strongly exothermic reaction had subsided, the mixture was allowed to stand overnight at room temperature. The mixture was then placed on a steam-bath for several hours to decompose excess peroxide and the solvent was removed under reduced pressure. The residual crystalline solid was recrystallized from ethanol, 9.67 g. (77.5%), m.p. 118–120°. Continued recrystallization from ethanol raised the m.p. to 121.5–123°.

Anal. Calcd. for $C_6H_{10}O_3S$: C, 44.43; H, 6.22; S, 19.77. Found: C, 44.46; H, 6.19; S, 19.87.

A 2,4-dinitrophenylhydrazone was prepared by the method of Shriner and Fuson.[12] Recrystallization from an ethanol–methylene chloride solution gave a m.p. 218–220°.

Anal. Calcd. for $C_{12}H_{14}N_4O_6S$: C, 42.10; H, 4.12. Found: C, 42.29; H, 4.30.

(B).—The combined filtrates of several diazotization reactions of amine acetate IVb, corresponding to 35.8 g. (0.15 mole), was concentrated to a volume of 200 ml. on a steam-bath. The aqueous solution was then extracted for three days continuously with methylene chloride. The methylene chloride was dried over anhydrous magnesium sulfate, the solvent removed on a steam-bath and the residual oil allowed to stand in a Dry Ice chest for several days whereupon crystallization took place, 3.3 g., m.p. 110–112°. Recrystallization from isopropyl alcohol raised the melting point to 121–122.5°. This compound was identical with the sample prepared as in procedure A.

4-Acetoxythiaepane 1,1-Dioxide (XIII).—To a solution of 37.0 g. (0.28 mole) of 4-hydroxythiaepane (X) in 300 ml. of glacial acetic acid, 65 ml. (0.57 mole) of 30% hydrogen peroxide was added in small portions with intermittent cooling in an ice-bath to moderate the reaction. After the strongly exothermic reaction had subsided, the mixture was allowed to stand overnight at room temperature. The reaction mixture was heated on a steam-bath for three hours in order to decompose the excess peroxide and the solvent was removed under reduced pressure. The residue was refluxed for 1 hour with an excess of acetyl chloride, the excess acetyl chloride distilled and the residue distilled through a Vigreux column to give 55.0 g. (95%) of a colorless liquid, b.p. 164–168° (0.4 mm.), which crystallized on cooling. Recrystallization from isopropyl alcohol gave a m.p. 75–76°.

Anal. Calcd. for $C_8H_{14}O_4S$: C, 46.58; H, 6.84; S, 15.54. Found: C, 46.54; H, 6.76; S, 15.63.

This compound also was obtained when 1.0 g. (0.0076 mole) of 4-hydroxythiaepane 1,1-dioxide (XII) was refluxed with an excess of acetyl chloride giving 1.5 g. (96%), m.p. 73–74.5°, of product. Recrystallization from isopropyl alcohol raised the m.p. to 75–76°. A mixed melting point with the previously characterized sample of 4-acetoxythiaepane 1,1-dioxide showed no depression, m.p. 73–75°.

4-Hydroxythiaepane 1,1-Dioxide (XII).—A mixture of 8.0 g. (0.049 mole) of 4-oxothiaepane 1,1-dioxide in 75 ml. of methanol was hydrogenated in the presence of *ca.* 1.0 g. of Raney nickel catalyst W_2 at 100 atmospheres and 100° for 2 hours. After removal of the catalyst, the mixture was evaporated on the steam-bath. The residual oil crystallized from isopropyl alcohol in the cold giving 6.4 g. (79.9%), m.p. 81–83°. Recrystallization from isopropyl alcohol gave a m.p. of 85–86.5°.

Anal. Calcd. for $C_6H_{12}O_3S$: C, 43.88; H, 7.37; S, 19.52. Found: C, 43.87; H, 7.42; S, 19.61.

3,5-Dibromothiaepane 1,1-Dioxide-4-one (XV).—To a solution of 7.5 g. (0.046 mole) of 4-oxothiaepane 1,1-dioxide (XII) in 5 ml. of glacial acetic acid was added 14.7 g. (0.092 mole) of bromine. The mixture was heated on a steam-bath until the vigorous evolution of hydrogen bromide subsided. The solvent was removed under reduced pressure and a white crystalline solid was obtained, 13.2 g. (90%), m.p. 138–144°. Several recrystallizations from small amounts of glacial acetic acid raised the melting point to 156.7–157.7°.

Anal. Calcd. for $C_6H_8Br_2O_3S$: C, 22.51; H, 2.52; Br, 49.95. Found: C, 22.39; H, 2.52; Br, 50.35.

Pyrolysis of Acetate XIII: Preparation of a Mixture of Δ^3- and Δ^4-Tetrahydrothiaepin 1,1-Dioxide (XIV).—Deacetylation was effected by refluxing 55.5 g. (0.27 mole) of the acetate XIII at the boiling point, *ca.* 300°, until no more acetic acid distilled. The residue was distilled through a Vigreux column to give 32.2 g. (82%) of a liquid, b.p. 120–125° (1.2 mm.), which crystallized immediately in the receiver. Recrystallization from ethanol gave white crystalline material, m.p. 83.5–88.5°.

Anal. Calcd. for $C_6H_{10}O_2S$: C, 49.20; H, 6.89; S, 21.90. Found: C, 49.22; H, 6.94; S, 21.96.

If the cracking procedure was carried out under milder conditions, a monoölefin, m.p. 107–112°, was obtained on repeated recrystallization from ethanol.

Addition of Bromine to Olefin XIV: Preparation of a Mixture of Dibromothiaepane 1,1-Dioxides (XVI).—To a solution of 10.0 g. (0.069 mole) of olefins XIV in 30 ml. of glacial acetic acid was added with cooling 11.0 g. (0.069 mole) of bromine. The product crystallized from solution and there was obtained 14.5 g. (69%) of dibromides, m.p. 97–101°. Repeated recrystallization of this material from carbon tetrachloride yielded a small amount of a sample which melted at 132–134°. Analysis of the substance melting at 97–101° and that melting at 132–134°, indicates that both are dibromides.

Anal. Calcd. for $C_6H_{10}Br_2O_2S$: C, 23.55; H, 3.29; Br, 52.20. Found: (m.p. 97–101°) C, 23.45; H, 3.16; Br, 52.30. Found: (m.p. 132–134°) C, 23.78; H, 3.17.

Dehydrohalogenation of Dibromide XVII. (A) Preparation of a Vinyl Bromide.—A solution of 1.3 g. (0.0043 mole) of the dibromide mixture, m.p. 97–101°, in 15 ml. of pyridine was refluxed for 2 hours. The cooled solution was diluted with 100 ml. of water, acidified with concentrated hydrochloric acid and extracted repeatedly with small portions of chloroform. The extract was dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated to dryness on a steam-bath to give 0.3 g. (31%) of a crystalline material, m.p. 130–139°. The compound gave no reaction with alcoholic silver nitrate at room temperature. Recrystallization from ethanol gave an analytical sample, m.p. 142–144°.

Anal. Calcd. for $C_6H_9BrO_2S$: C, 32.01; H, 4.03. Found: C, 32.10; H, 4.12.

(B) Preparation of a Mixture of Dimethylamine Bromides.—Into a warm solution of 1.0 g. (0.0033 mole) of the dibromide mixture, m.p. 97–101°, in 50 ml. of benzene was passed a stream of anhydrous dimethylamine. At the initiation of the addition a white precipitate of dimethylamine hydrobromide was formed. The mixture was cooled, the precipitate removed by filtration and the filtrate evaporated to dryness on a steam-bath to give 0.15 g. (16.9%), m.p. 197–199° dec. Recrystallization from methanol gave a m.p. 198–200° dec.

Anal. Calcd. for $C_8H_{16}BrNO_2S$: C, 35.56; H, 5.96; N, 5.19. Found: C, 35.59; H, 5.94; N, 5.05.

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