(63%) of product, m.p. 126.5–128°. Sarel[14] reports m.p. 126° for the cyclic carbonate prepared from hydrobenzoin.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.98; H, 5.04. Found: C, 75.19; H, 4.88.

***trans*-4,5-Diphenyl-1,3-dioxolan-2-one.**—*dl*-Hydrobenzoin, prepared by the sequence *trans*-stilbene → *meso*-stilbene dibromide (Br_2)[24] → *dl*-hydrobenzoin monoacetate (silver acetate–wet glacial acetic acid) → *dl*-hydrobenzoin (sodium hydroxide–ethanol[25]), was converted in 74% yield by the prior procedure to the *trans* cyclic carbonate, m.p. 110–111.5°.

Anal. Found: C, 75.11; H, 5.11.

***dl*-Butadiene-1,2:3,4-bis(trithiocarbonate) (VII).**—A solution of 21.51 g. (0.25 mole) of *dl*-butadiene dioxide (obtained from the Koppers Co., Pittsburgh, Pa.) in 25 ml. of methanol was added over 10 min. to a stirred solution of 70.13 g. (1.25 moles) of potassium hydroxide and 114.21 g. (1.4 moles) of carbon disulfide in 325 ml. of methanol cooled to 0–5°. After about one-half of the dioxide was added, gentle reflux occurred and a precipitate formed. The mixture was kept at room temperature for 64 hr. The precipitate was filtered, washed with several portions of water, and dried *in vacuo* at room temperature. The product, 36.48 g. (54%), did not melt, but changed from yellow to orange to red to a black tar at 225–235°. It was insoluble in refluxing dimethylformamide, benzene, acetone, ether, and tetrahydrofuran, but dissolved readily in concentrated sulfuric acid at room temperature. The sulfuric acid solution was poured into ice–water and the precipitated product, after washing and drying, had an infrared spectrum which was identical with the original compound. The infrared spectrum showed only one absorption band in the C=S stretching region at 1052 cm.$^{-1}$ (Nujol).

Anal. Calcd. for $C_6H_6S_6$: C, 26.64; H, 2.24; S, 71.12. Found: C, 26.94; H, 2.48; S, 70.82.

***dl*-1,2,3,4-Butanetetrathiol.**—To 3.80 g. (0.1 mole) of lithium aluminum hydride in 175 ml. of anhydrous ether was added 5.41 g. (0.02 mole) of the bistrithiocarbonate (VII) in small portions over 10 min. with stirring. Immediately thereafter the reaction mixture began to reflux vigorously. After 19 hr. at room temperature all of the yellow solid had reacted. The mixture was cooled to 0° and water was added (caution) to decompose the excess hydride. After acidifying with cold 6 *N* hydrochloric acid, the ether layer was separated and washed with two 100-ml. portions of 10% aqueous sodium bicarbonate, two 50-ml. portions of water, dried over anhydrous sodium sulfate, and filtered. The ether was distilled *in vacuo* at room temperature. Fractional distillation of the residual oil, 4.03 g., yielded 1.57 g. (42%) of a water white liquid, b.p. 131–132° (0.6 mm.).

Infrared analysis revealed a high-intensity mercaptan absorption band at 2550 cm.$^{-1}$ (pure liquid).

Anal. Calcd. for $C_4H_{10}S_4$: C, 25.78; H, 5.40; S, 68.82. Found: C, 25.70; H, 5.80; S, 68.41.

The tetraacetate, prepared as before, had m.p. 87–88.5°.

Anal. Calcd. for $C_{12}H_{18}O_4S_4$: C, 40.65; H, 5.12; S, 36.18. Found: C, 40.83; H, 5.31; S, 35.90.

Acknowledgment.—We wish to acknowledge gratefully support of this work by the National Institutes of Health under Grant No. AI-01425-09.

---

[24] L. I. Smith and M. M. Falkof, "Organic Synthesis," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 350.

[25] Reference 23, p. 189.

Seven-Membered Heterocycles. II. The Reactions of Benzo[*b*]thiepin 1,1-Dioxide[1-3]

VINCENT J. TRAYNELIS AND RICHARD F. LOVE[4]

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

Received August 8, 1963

The light-catalyzed addition of 1 or 2 moles of bromine to benzo[*b*]thiepin 1,1-dioxide proceeded on the heterocyclic ring, while attempted additions of piperidine and hydrogen bromide failed. Electrophilic nitration of I gave two mononitro derivatives with substitution taking place on the benzene ring. The nitration of 2,3-dihydrobenzo[*b*]thiepin 1,1-dioxide formed an adduct which decomposed to 4-nitrobenzo[*b*]thiepin 1,1-dioxide.

In a previous paper[1] the literature of thiepin chemistry was reviewed and the synthesis of benzo[*b*]thiepin 1,1-dioxide described. This report deals with the chemical properties of that compound, in particular, thermal stability, the addition of bromine, and the effects of electrophilic and nucleophilic reagents.

When benzo[*d*]thiepin-2,4-dicarboxylic acid was placed in refluxing ethanol, sulfur and naphthalene-2,3-dicarboxylic acid resulted,[5,6] while benzo[*d*]thiepin 3,3-dioxide required elevated temperatures for conversion to naphthalene.[7] Unlike these materials benzo[*b*]thiepin 1,1-dioxide, a colorless crystalline solid, was stable in refluxing ethanol and distilled with slight decomposition when inserted into a Wood's metal bath at 250°; however, when it was refluxed in diethylcarbitol for several hours, resinification took place. In no experiment was naphthalene detected.

Thianaphthene sulfone undergoes facile nucleophilic additions with a variety of reagents such as piperidine, diethylamine, and hydrogen bromide to cite a few examples.[8] The product formed in each reaction is the 3-substituted (3-piperidino, 3-diethylamino, 3-bromo) 2,3-dihydrothianaphthene sulfone. When benzo[*b*]thiepin 1,1-dioxide was allowed to react with piperidine or with concentrated hydrobromic acid under conditions which resulted in addition to thianaphthene sulfone,[8] no reaction was observed and good recoveries of starting benzo[*b*]thiepin 1,1-dioxide were made. These observations indicate that the heterocyclic ring of benzo[*b*]thiepin 1,1-dioxide does not behave as an ordinary α,β-unsaturated sulfone.

While 2,3-dihydrobenzo[*b*]thiepin 1,1-dioxide added bromine readily in both warm chloroform or glacial acetic acid, the reaction of benzo[*b*]thiepin 1,1-dioxide (I) with bromine occurred only in the presence of sunlight or ultraviolet light. Addition of 1 mole of bromine produced a dibromide (II) in 71% yield which could add a 2nd mole of bromine to form a tetrabromide (III) (60% yield). Alternately, the tetrabromide was formed by the addition of 2 moles of bromine to I (84% yield).

---

[1] For paper I in this series, see V. J. Traynelis and R. F. Love, *J. Org. Chem.*, **26**, 2728 (1961).

[2] Presented in part at the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[3] Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

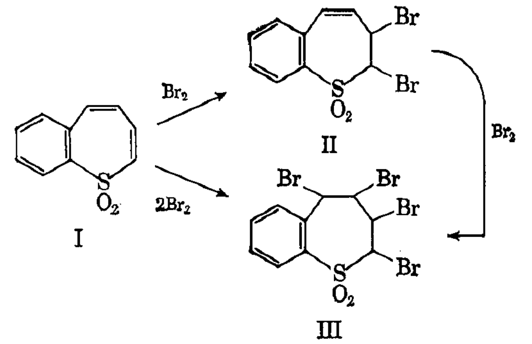
[4] Socony Mobil Fellow 1956–1957; Eastman Kodak Fellow 1957–1958; abstracted from part of the Ph.D. dissertation of R. F. Love, June, 1960.

[5] G. P. Scott, *J. Am. Chem. Soc.*, **75**, 6332 (1953).

[6] K. Dimroth and G. Lenke, *Ber.*, **89**, 2608 (1956).

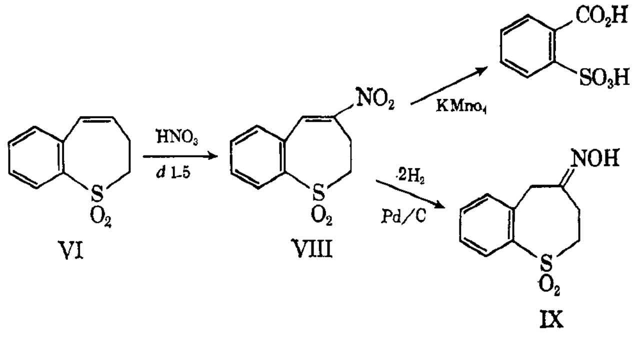
[7] W. E. Truce and F. J. Lotspeich, *J. Am. Chem. Soc.*, **78**, 848 (1956).

[8] F. G. Bordwell and W. H. McKellin, *ibid.*, **72**, 1985 (1950).



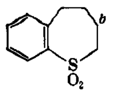
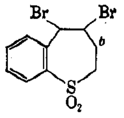
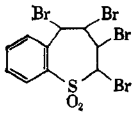
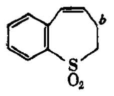
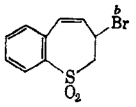
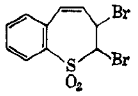
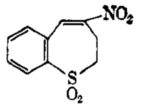
The structural assignment of the tetrabromide as 2,3,4,5-tetrabromo-2,3,4,5-tetrahydrobenzo[*b*]-thiepin 1,1-dioxide (III) was based primarily on a comparison of the ultraviolet spectrum with model compounds. Table I contains a listing of these data which clearly show a similarity between III and other 2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxides. In the case of the dibromide one must consider that the addition of 1 mole of bromine to I may proceed by 1,2-addition to produce II or 4,5-dibromo-4,5-dihydrobenzo-[*b*]thiepin 1,1-dioxide or by 1,4-addition forming 2,5-dibromo-2,5-dihydrobenzo[*b*]thiepin 1,1-dioxide. Examination of the ultraviolet spectra in Table I clearly points to a styrene-like chromophore which requires structure II for the dibromide.

The study of nitration as an example of electrophilic substitution was initiated with 2,3-dihydrobenzo[*b*]-thiepin 1,1-dioxide (VI) which formed a mononitro derivative in yields ranging from 50 to 64%. Upon oxidation this nitro compound gave *o*-sulfobenzoic acid isolated and identified as the S-benzylthiouronium salt, m.p. 204–205° (lit.[9] m.p. 205–206°). A mixture melting point with an authentic sample was not depressed. A quantitative semimicro hydrogenation of the nitro derivative stopped after the absorption of 2 moles of hydrogen with the formation of the oxime (IX). This oxime, m.p. 186–187°, differed from the oxime of 5-oxo-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide, m.p. 199–200°, and had an n.m.r. spectrum (see Experimental section) which was consistent with the assigned structure IX. These data provided evidence that the nitro group entered the heterocyclic ring and was attached to C-4 as shown in structure VIII. Supporting evidence of this assignment was found in the ultraviolet spectrum of VIII (see Table I) showing the presence of a β-nitrostyrene chromophore.



Although attachment of the nitro group to an olefinic position was unexpected, the literature[10] contains examples of nitration of olefins to produce nitroolefins.

TABLE I.—ULTRAVIOLET SPECTRA

Compound	λ_{max}, mμ	log ϵ	Solvent
 IV	270 277	3.15 3.15	Dioxane
 V	(267)[a] 274 (281)[a]	3.30 3.35 3.29	Dioxane
 III	277 (284)[a]	3.34 3.30	Dioxane
 VI	<224 250 291	 3.99 3.74	95% ethanol
 VII	224 261 294 (302)[a]	 3.86 3.78 3.73	95% ethanol
 II	230 259 296	3.48 3.23 3.13	95% ethanol
IV	262 269 277	3.51 3.56 3.54	95% ethanol
III	278 284	3.54 3.51	95% ethanol
$C_6H_5SO_2CH{=}CH_2$[c]	225 267	4.1 3.02	95% ethanol
 VIII	225 311	3.00 3.10	95% ethanol
$C_6H_5CH{=}CHNO_2$[d]	227 309	3.98 4.22	95% ethanol
$C_6H_5CH{=}C(NO_2)CH_3$[d]	226 305	4.00 4.09	95% ethanol

[a] Shoulder. [b] See ref. 1. [c] C. C. Price and H. Morita, *J. Am. Chem. Soc.*, **75**, 4747 (1953). [d] E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.*, 1104 (1947).

In the reaction of VI with red fuming nitric acid an intermediate adduct was isolated. This material melted over a range 60–80°, appeared unstable, and decomposed at temperatures over 110° with the evolution of a gas. The infrared spectrum contained bands which could be attributed to sulfone,[11] nitro,[12] and nitrite[13] functions. Nitrate esters did not appear likely due to the absents of strong absorption between 6.0 and 6.2 μ and in the region of 13.3 μ.[12] These data suggest that the intermediate adduct is a 4-nitro-5-nitrite derivative, although one cannot exclude the presence of some of the 4,5-dinitro derivative. The nature of this addition reaction is not clear at this time.

When 2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide (X) was treated with red fuming nitric acid, a mononitro derivative was isolated in 64% yield. This substance was assigned the structure 8-nitro-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide (XI) on the

---

[9] S. Veibel and H. Lillelund, *Bull. soc. chim. France*, [5] **5**, 1153 (1938).

[10] R. Anschutz and A. Hilbert, *Ber.*, **54**, 1854 (1921); H. Wieland and F. Rahn, *ibid.*, 1770 (1921); J. Mauthner and W. Suida, *Monatsh.*, **24**, 648 (1903).

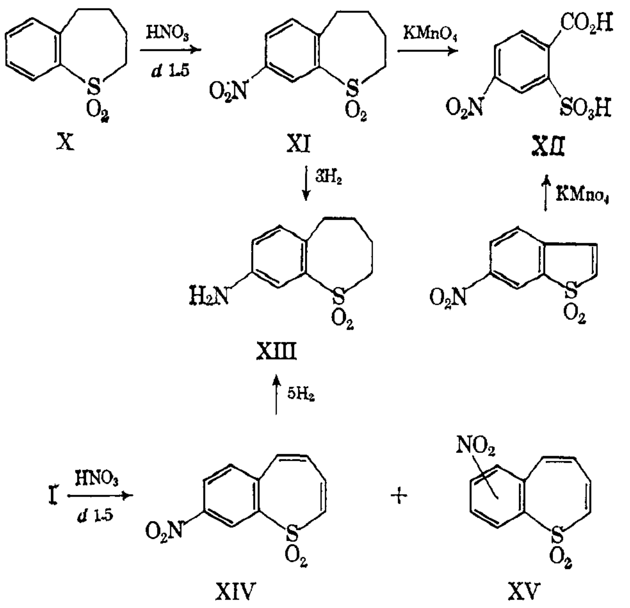
[11] K. C. Schriber, *Anal. Chem.*, **21**, 1168 (1949).

[12] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

[13] P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1952).

basis of its oxidation to 4-nitro-2-sulfobenzoic acid (XII) isolated as the S-benzylthiouronium salt. An authentic sample of this derivative was prepared by the oxidation of 6-nitrothianaphthene.[14]

The nitration of benzo[*b*]thiepin (I) under similar conditions produced two isomeric mononitro derivatives, separated by column chromatography. The isomer melting at 180–181° (45% yield) absorbed 5 moles of hydrogen and gave an amine whose infrared spectrum was identical with that of amine XIII obtained by reduction of XI. Therefore, the structure assigned to this isomer is 8-nitrobenzo[*b*]thiepin 1,1-dioxide (XIV). No structural assignment has been established for the other isomer (XV), m.p. 185–186 (31% yield); however, in view of the directive effects of the sulfone group, a vinyl group, and the position of substitution in compound XIV, isomer XV is probably 6-nitrobenzo[*b*]thiepin 1,1-dioxide.



In review of our studies of benzo[*b*]thiepin 1,1-dioxide, one can summarize the chemical properties as (1) the failure of thermal extrusion to produce naphthalene, (2) the failure of nucleophilic additions to the heterocyclic ring, (3) light-catalyzed addition of 1 or 2 moles of bromine to the heterocyclic ring, (4) the attack of the heterocyclic ring by potassium permanganate, and (5) the electrophilic substitution of nitration proceeds in the benzene ring *meta* with respect to the sulfone group. These results suggest appreciable olefinic character of the bonds in the heterocyclic ring.

Experimental[15]

Benzo[*b*]thiepin 1,1-Dioxide.—This compound, m.p. 139–140°, was available from the synthesis described previously.[1]

Thermal Stability of Benzo[*b*]thiepin 1,1-Dioxide.—Benzo[*b*]thiepin 1,1-dioxide was recovered unchanged after 20 hr. of reflux in 95% ethanol; however, when refluxed in diethylcarbitol (b.p. 183°) under nitrogen for 12 hr., only a dark resinous material separated upon dilution with water.

A flask fitted with a cold-finger, nitrogen inlet tube and an outlet attached to a solution of sodium hydroxide was charged with benzo[*b*]thiepin 1,1-dioxide (102 mg., 0.53 mmole). When the flask was immersed in a Wood's metal bath at 250° which was slowly raised to 280°, 80 mg. (79%) of benzo[*b*]thiepin 1,1-dioxide, m.p. 137–139° (infrared spectrum identical with authentic sample), collected on the cold finger. Above 280° the small residue resinified rapidly.

The sodium hydroxide solution was treated with 5 ml. of 30% hydrogen peroxide and acidified with nitric acid; the addition of barium nitrate solution gave 10 mg. (8%) of barium sulfate.

2,3-Dibromo-2,3-dihydrobenzo[*b*]thiepin 1,1-Dioxide.—A solution of bromine (200 mg., 1.25 mmoles) and benzo[*b*]thiepin 1,1-dioxide (234 mg., 1.22 mmoles) in 10 ml. of glacial acetic acid was decolorized after exposure to ultraviolet light for 30–45 min. or more quickly when exposed to sunlight. After the slightly yellow solution was poured into water containing a small amount of sodium bisulfite, the precipitate was collected, and crystallization from acetone gave 305 mg. (71%) of dibromide, m.p. 147–148°.

Anal. Calcd. for $C_{10}H_8Br_2O_2S$: C, 34.12; H, 2.29. Found: C, 34.30; H, 2.67.

2,3,4,5-Tetrabromo-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-Dioxide.—A solution of benzo[*b*]thiepin 1,1-dioxide (103 mg., 0.53 mmole) and bromine (180 mg., 1.13 mmoles) in 10 ml. of glacial acetic acid was exposed to ultraviolet light for 1 hr. and processed as described before. Crystallization from dioxane gave 227 mg. (84%) of the tetrabromide, m.p. 222° dec.

Anal. Calcd. for $C_{10}H_8Br_4O_2S$: C, 23.46; H, 1.57. Found: C, 23.80; H, 1.81.

The dibromide (109 mg., 0.31 mmole) from the previous experiment was treated with 70 mg. (0.44 mmole) of bromine and the reaction processed as described before. The yield of the tetrabromide, m.p. 220° dec., was 96 mg. (60%). A mixture melting point with this tetrabromide was not depressed and both infrared spectra were identical.

Attempted Reaction of Benzo[*b*]thiepin 1,1-Dioxide with Piperidine.—A blend of 111 mg. (0.57 mmole) of benzo[*b*]thiepin 1,1-dioxide, 98 mg. (1.15 mmoles) of piperidine, and 5.0 ml. of absolute ethanol was refluxed 30 min. and evaporation under a stream of nitrogen afforded a quantitative recovery of the starting material, m.p. 138–140°.

Attempted Reaction of Benzo[*b*]thiepin 1,1-Dioxide with Hydrobromic Acid.—Benzo[*b*]thiepin 1,1-dioxide (105 mg., 0.54 mmole) in 4 ml. of 48% hydrobromic acid was refluxed for 30 min. and upon cooling deposited 91 mg. (87%) of unchanged starting material, m.p. 139–140°.

Nitration of 2,3-Dihydrobenzo[*b*]thiepin 1,1-Dioxide.—A solution of 500 mg. (2.58 mmoles) of 2,3-dihydrobenzo[*b*]thiepin 1,1-dioxide in 25 ml. of nitric acid (*d* 1.5) was kept at 5–10° for 20–30 min., poured into water, and the solid filtered. Slow crystallization of this solid from acetone gave 390 mg. (64%) of 4-nitro-2,3-dihydrobenzo[*b*]thiepin 1,1-dioxide, m.p. 197–198°.

Alternately, this diluted acid solution was heated at 80–85° for 0.5 to 1 hr. Upon cooling the same nitroolefin crystallized as pale yellow needles.

Anal. Calcd. for $C_{10}H_9NO_4S$: C, 50.20; H, 3.79. Found: C, 50.11; H, 4.04.

In another experiment the precipitate from dilution of the reaction mixture was collected and air-dried. It appeared unstable on standing, melted at 60–80°, and decomposed at temperatures over 110° with the evolution of a gas. A sample was suspended in dilute sulfuric acid and after short warming gave nitrous acid. The infrared spectrum (potassium bromide disk) showed strong absorption at (all values listed as μ) 2.4,[16] doublet 2.7, 2.76,[16] 3.3, 4.2, 5.96, 6.37, 6.56, 6.75, 7.0, 7.51, 7.65, 7.80, 8.14, 8.35, 8.57, 8.71, 8.91, 9.4, 9.6, 10.8, 11.75, 12–12.5 broad, 1.4–14.7 broad, and 15.2.

Oxidation of 4-Nitro-2,3-dihydrobenzo[*b*]thiepin 1,1-Dioxide.—A mixture of 4-nitro-2,3-dihydrobenzo[*b*]thiepin 1,1-dioxide (500 mg., 2.1 mmoles), potassium hydroxide (600 mg., 10.0 mmoles), potassium permanganate (3.0 g., 19 mmoles) in 35 ml. of water was heated on a steam plate for 6 hr. After cooling the excess potassium permanganate was destroyed with 30% hydrogen peroxide and the solution acidified with hydrochloric acid, fil-

---

[14] F. Challenger and P. H. Clapham, *J. Chem. Soc.* 1615 (1948).

[15] All melting points are uncorrected. The microanalyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were determined with a Perkin-Elmer Model 21 or a Baird Associates infrared spectrophotometer by R.F.L. and Anthony Saraceno. The n.m.r. spectra were measured with a Varian Associates 60-Mc. high resolution n.m.r. spectrometer, Model V-4300-B.

[16] Reference 13 contains a reproduction of the infrared spectrum of methyl nitrite and shows bands at 2.2, 3.0 and 3.1, 3.4, 4.0, 4.4 μ, and others.

tered, made nearly neutral, and concentrated to 30 ml. The addition of 500 mg. (2.5 mmoles) of S-benzylthiouronium chloride in 5 ml. of water gave a precipitate which was filtered and recrystallized from aqueous ethanol. The yield of the S-benzylthiouronium salt of *o*-sulfobenzoic acid, m.p. 204–206° (lit.[9] m.p. 205–206°) was 0.50 g. (41%). A mixture melting point with authentic material was not depressed.

Hydrogenation of 4-Nitro-2,3-dihydrobenzo[*b*]thiepin 1,1-Dioxide.—A stirred mixture of 4-nitro-2,3-dihydrobenzo[*b*]thiepin (110.7 mg., 0.465 mmole) dissolved in 10 ml. of freshly distilled dioxane and 17 mg. of 10% palladium–charcoal was exposed to hydrogen at atmospheric pressure in a semimicro hydrogenation apparatus.[17]

When 0.95 mmole of hydrogen was absorbed, the reaction appeared to stop. After the catalyst was filtered and the solvent evaporated, the residue was crystallized from ethanol with a charcoal treatment and gave 71.4 mg. (68%) of 4-oxo-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide oxime, m.p. 183–184°. Repeated crystallizations from an ethyl acetate and petroleum ether (b.p. 30–60°) mixture gave an analytical sample, m.p. 186–187°.

Anal. Calcd. for $C_{10}H_{11}NO_3S$: C, 53.32, H, 4.92. Found: C, 53.38, 53.53; H, 5.26, 5.18.

The n.m.r. spectrum[18] had the following peaks: singlet, τ 5.06 (hydroxyl proton); singlet, 5.57 (benzylic proton); multiplet, center 6.48; multiplet, center 6.97 (these peaks are attributed to the protons α to the sulfone and oxime functions).

In a second experiment 1.04 g. (4.37 mmoles) of the nitro compound in 40 ml. of dioxane was reduced to 0.79 g. (81%) of the oxime, m.p. 182–183°, in the same apparatus using 36 mg. of platinum oxide catalyst and hydrogen at atmospheric pressure.

The reaction was also carried out in 76% yield using a Paar hydrogenation apparatus and 10% palladium–charcoal catalyst.

5-Oxo-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-Dioxide Oxime.—The reaction of 5-oxo-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide (1.0 g., 4.75 mmoles) and hydroxylamine hydrochloride (1.0 g., 14.4 mmoles) in 6 ml. of pyridine and 6 ml. of absolute ethanol for 3 hr. on a steam bath produced 0.95 g. (89%) of the oxime, m.p. 195–197°. An analytical sample, m.p. 199–200°, was obtained by repeated recrystallization from ethanol.

Anal. Calcd. for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92. Found: C, 53.72, 53.60; H, 5.06, 5.01.

The n.m.r. spectrum[18] had the following peaks: singlet, 4.94 (hydroxyl proton); triplet, center 6.32; triplet, center 6.63 (these peaks are attributed to the protons α to the sulfone and oxime functions); multiplet, center 7.73 τ (C-3 methylene protons).

Nitration of 2,3,4,5-Tetrahydrobenzo[*b*]thiepin 1,1-Dioxide.—A solution of 2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide (0.94 g., 0.47 mmole) in 20 ml. of nitric acid (*d* 1.5) was kept at 5–10° for 1 hr. and upon dilution with water gave 923 mg. (80%) of crude nitro compound, m.p. 184–190°. Crystallization from benzene gave 735 mg. (64%) of 8-nitro-2,3,4,5-tetrahydrobenzo-[*b*]thiepin 1,1-dioxide, m.p. 197–198°, as fine white needles. An analytical sample, m.p. 198°, was obtained by recrystallization from benzene and from absolute ethanol.

Anal. Calcd. for $C_{10}H_{11}NO_4S$: C, 49.78; H, 4.59. Found: C, 49.74, 49.87; H, 4.64, 4.81.

Hydrogenation of 8-Nitro-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-Dioxide.—After a mixture of 8-nitro-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide (1.2 g., 5.0 mmoles) in 50 ml. of dioxane and 10% paladium–charcoal (100 mg.) was exposed to 40 lb. of hydrogen pressure for 1 hr. in a Paar hydrogenation apparatus, the mixture was filtered, the solvent evaporated from the filtrate, and the residue taken up in 20% hydrochloric acid. The acidic solution was treated with decolorizing charcoal, filtered, and divided into two parts. To one part was added 3 g. of sodium acetate and 2 ml. of acetic anhydride and upon rapid stirring a crystalline precipitate formed. After filtration, crystallization from ethanol gave 0.32 g. (25% based on the starting nitro compound) of 8-acetamido-2,3,4,5-tetrahydrobenzo[*b*]-thiepin 1,1-dioxide, m.p. 224–225°.

Anal. Calcd. for $C_{12}H_{15}NO_3S$: C, 56.89; H, 5.97. Found: C, 57.06; H, 5.93.

The other part of the acidic solution was made alkaline and gave 0.34 g. (32%) of 8-amino-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide, m.p. 169–170°. An analytical sample was prepared by recrystallization from ethanol.

Anal. Calcd. for $C_{10}H_{13}NO_2S$: C, 56.84; H, 6.20. Found: C, 56.62; H, 6.26.

Oxidation of 8-Nitro-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-Dioxide.—A suspension of 300 mg. (1.25 mmoles) of 8-nitro-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide in a solution of 400 mg. (7.1 mmoles) of potassium hydroxide in 25 ml. of water was heated to gentle reflux and 1.5 g. (9.5 mmoles) of potassium permanganate was added in small portions over 5 hr. After cooling, the mixture was acidified with concentrated hydrochloric acid, treated with 4 ml. of 30% hydrogen peroxide, and filtered. After the filtrate was adjusted to pH 5, the solution was concentrated until precipitation began. The solid was dissolved by addition of water and the solution treated with 300 mg. (1.5 mmoles) of S-benzylthiouronium chloride in 3 ml. of water. A crystalline product was formed and crystallization of this substance from 50% aqueous ethanol gave 107 mg. (16%) of the S-benzylthiouronium salt of 4-nitro-2-sulfobenzoic acid, m.p. 240.5–242°. A mixture melting point with the salt obtained from the oxidation of 6-nitrothianaphthene showed no depressions and the infrared spectra of the two samples were identical.

6-Nitrothianaphthene Sulfone.—Using the procedure of Bordwell, Lampbert, and McKellin,[19] thianaphthene was oxidized to thianaphthene sulfone, m.p. 140–142° (lit.[19] m.p. 142–143°), in 70% yield and nitration of the sulfone by the method of Challenger and Clapham[14] produced 6-nitrothianaphthene sulfone, m.p. 187–188° (lit.[14] m.p. 188°).

Oxidation of 6-Nitrothianaphthene Sulfone.—The previous procedure for oxidation of 8-nitro-2,3,4,5-tetrahydrobenzo[*b*]-thiepin 1,1-dioxide was employed with 500 mg. (2.4 mmoles) of 6-nitrothianaphthene sulfone, 400 mg. (7.1 mmoles) of potassium hydroxide in 35 ml. of water and 1.2 g. (7.6 mmoles) of potassium permanganate. After 2 days at 40°, 103 mg. of unchanged sulfone was recovered along with 382 mg. (44%) of the S-benzylthiouronium salt of 4-nitro-2-sulfobenzoic acid, m.p. 242–243°.

Anal. Calcd. for $C_{23}H_{25}N_5S_3O_7$: C, 47.64; H, 4.35. Found: C, 47.81; H, 4.45.

Nitration of Benzo[*b*]thiepin 1,1-Dioxide.—Benzo[*b*]thiepin 1,1-dioxide (207 mg., 108 mmoles) was added in small portions with stirring to 8 ml. of nitric acid (*d* 1.5) at 5–10°. After this solution was kept at 5–15° for 45 min. and poured into ice-water and the precipitate was filtered and quickly crystallized from acetone. The yield of the yellow crystalline nitro derivative (mixture of two isomers), m.p. 146–160°, was 167 mg. (65%).

Anal. Calcd. for $C_{10}H_7NO_4S$: C, 50.62; H, 2.97. Found: C, 50.59; H, 3.16.

In a second experiment the reaction of 309 mg. (1.61 mmoles) of benzo[*b*]thiepin 1,1-dioxide and 13 ml. of nitric acid (*d* 1.5) was processed as before and the crude precipitate dried, dissolved in 20 ml. of benzene, and placed on 75 g. of Alcoa activated alumina F-20. With 90% benzene–10% ether as eluent, 119 mg. (31%) of (?)-nitrobenzo[*b*]thiepin 1,1-dioxide was collected. Solutions of this material turned purple upon prolonged exposure to light. An analytical sample, m.p. 185–186°, was prepared by repeated recrystallization from absolute ethanol.

Anal. Calcd. for $C_{10}H_7NO_4S$: C, 50.62; H, 2.97. Found: C, 50.23; H, 3.16.

A second fraction which was eluted with 70% benzene–30% ether was 177 mg. (46%) of 8-nitrobenzo[*b*]thiepin 1,1-dioxide, m.p. 180–181°. Several recrystallizations from absolute ethanol failed to raise the melting point.

Anal. Calcd. for $C_{10}H_7NO_4S$: C, 50.62; H, 2.97. Found: C, 50.29; H, 3.18.

Hydrogenation of 8-Nitrobenzo[*b*]thiepin 1,1-Dioxide.—A stirred mixture of 8-nitrobenzo[*b*]thiepin 1,1-dioxide (41 mg., 0.17 mmole) dissolved in 5 ml. of freshly distilled dioxane and 10 mg. of 10% palladium–charcoal was exposed to hydrogen at atmospheric pressure in a semimicro hydrogenation apparatus.[17] After 0.84 mmole of hydrogen was absorbed, the catalyst was filtered, washed, and the solvent evaporated. The residue, m.p. 162–165°, was 21 mg., 66%, and had an infrared spectrum identical with that of 8-amino-2,3,4,5-tetrahydrobenzo[*b*]thiepin 1,1-dioxide.

---

(17) For a diagram of the apparatus, see A. A. Baldoni, Ph.D. dissertation, University of Notre Dame, 1951, p. 54.

(18) The n.m.r. spectra were recorded in pyridine using tetramethylsilane as an internal standard. Only the aliphatic and hydroxylic protons were considered.

(19) F. G. Bordwell, B. B. Lampbert, and W. H. McKellin, *J. Am. Chem. Soc.*, **71**, 1702 (1949).