# Seven-Membered Heterocycles. IV. The 5-Hydroxy-2-chloro-4,5-dihydro-1-benzothiepin System[1a,b]

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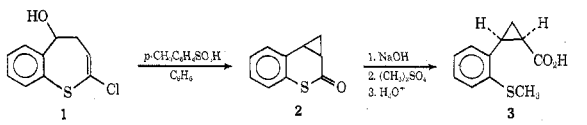
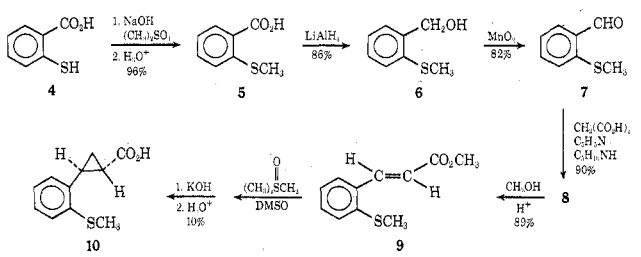
The synthesis of *trans*-2-(2-methylthiophenyl)cyclopropanecarboxylic acid (**10**) is described with the use of dimethyloxosulfonium methylide to introduce the cyclopropane ring into methyl *trans*-*o*-methylthiocinnamate. Acid-catalyzed dehydration of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1,1-dioxide gave 2-chloro-1-benzothiepin 1,1-dioxide, while reaction of *p*-toluenesulfonic acid and 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1-oxide produced 1-chloronaphthalene. The latter product is explained by SO elimination from the dehydration product, 4-chloro-1-benzothiepin 1-oxide.

In a previous report[1a] we described the acid-catalyzed conversion of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin (**1**) to 2-oxo-1a,7b-dihydrocyclopropa[*c*][1]benzothiapyran (**2**) instead of the expected 2-chloro-1-benzothiepin. A portion of the chemical evidence for **2** involved its conversion by alkali and dimethyl sulfate into *cis*-2-(methylthiophenyl)cyclopropanecarboxylic acid (**3**). Additional support for these structural



assignments is now presented with the synthesis of the *trans*-cyclopropanecarboxylic acid **10**. Also the action of acid on the sulfoxide and sulfone of **1** is reported.

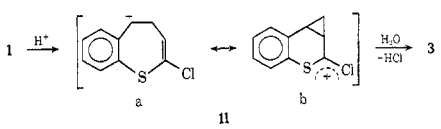
The reaction sequence outlined below[2] led to the synthesis of *trans*-2-(2-methylthiophenyl)cyclopropanecarboxylic acid (**10**). Oxidation of *o*-(methylthio)benzyl



alcohol (**6**) to *o*-(methylthio)benzaldehyde (**7**) was effected by $MnO_2$[3] (82%) or $CrO_3 \cdot 2C_5H_5N$[4] (54%) while the Doebner modification[5] of the Knoevenagel reaction (90%) was utilized in the conversion of **7** to *o*-(methylthio)cinnamic acid (**8**). The methyl ester **9** was assigned the trans configuration from the nature of the cinnamic acid synthesis and the coupling constant $J$ = 15 Hz for the olefinic protons in **9**. Introduction of the cyclopropane ring utilized Corey's method[6] of methylene transfer to a cinnamic acid ester which proceeds stereoselectively to the trans-2-phenylcyclopropanecarboxylic acid ester.[7,8] The reaction of dimethyloxosulfonium methylide with **9** gave a mixture of esters which were saponified and upon fractional crystallization provided *trans*-2-(2-methylthiophenyl)-cyclopropanecarboxylic acid (**10**) in 10% overall yield.

Mohrbacher and Cromwell[9] have described a spectral method to distinguish *cis*- and *trans*-2-phenylcyclopropanecarboxylic acid; however, the uv spectral properties of **10** [$\lambda_{max}$ 252 m$\mu$ (log $\epsilon$ 3.94)] and **3** [$\lambda_{max}$ 253 m$\mu$ (log $\epsilon$ 3.94)][1] were so similar that assignment of geometric structure was not possible. In addition **10** and **3** had similar carbonyl and hydroxyl frequencies in the infrared spectra. The nmr spectra of **10** and **3** were complex and the region where the $C_1$ H ($\alpha$ to $CO_2H$) absorbs also contains the methyl resonance. However, the position of the $C_1$ H band is at lower field for **10** ($\tau$ 7.10–7.45) than for **3** ($\tau$ 7.45–7.92), which is similar to the $C_1$ H in *trans*- and *cis*-2-phenylcyclopropanecarboxylic acid. These data support the structural similarly of **10** and **3**; however, the strength of the stereochemical assignment resides in the synthetic origin of **10** and **3**[1] with some support from the nmr spectra. An attempt to isomerize the cis acid **3** to trans acid **10** by refluxing **3** in potassium *tert*-butoxide and *tert*-butyl alcohol for 7 days gave only starting cis acid **3**.

The proposed intermediate in the acid-catalyzed conversion of **1** to **2** is a homoallylic cation[1a] (**11**). We



were interested in observing the effect of changing the nature of the electron-donating sulfur in **1** to electron-withdrawing sulfoxide or sulfone groups on the acid-catalyzed reaction. Such electron-withdrawing groups should destabilize structures like **11b** and reduce the amount of rearrangement.

Sulfoxide **12** was obtained by oxidation of **1** with perbenzoic acid in the presence of $BF_3$ under careful temperature control (−10°). When elevated temperatures or longer reaction times are used, oxidation proceeds further to form sulfone **13**. Structural assignments for sulfoxide **12** and sulfone **13** were based on

(1) (a) For part III in this series see V. J. Traynelis and J. R. Livingston, Jr., *J. Org. Chem.*, **29**, 1092 (1964). (b) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research. (c) To whom correspondence should be sent: Department of Chemistry, West Virginia University, Morgantown, W. Va. 26506. (d) Abstracted from a portion of the Ph.D. Dissertation submitted by D. M. B. in August 1968.

(2) Preparation of compounds **5**, **6**, and **7** was accomplished independently and prior to the literature reports cited below. In each of these cases the yields reported in this work exceed those published.

(3) E. F. Pratt and J. F. van de Castle, *J. Org. Chem.*, **26**, 2973 (1961).

(4) J. R. Holum, *ibid.*, **26**, 4814 (1961).

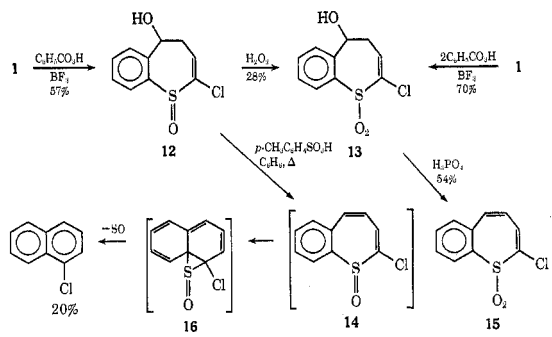
(5) O. Doebner, *Chem. Ber.*, **33**, 2140 (1900).

(6) E. J. Corey and M. Chaykovsky, *Tetrahedron Lett.*, 169 (1963). We have also observed that reaction of dimethyloxosulfonium methylide with methyl cinnamate gave a 39% yield of methyl *trans*-2-phenylcyclopropanecarboxylate.

(7) S. R. Landor and N. Punja, *J. Chem. Soc. C*, 2495 (1967).

(8) C. Kaiser, B. M. Trost, J. Beeson, and W. Weinstock, *J. Org. Chem.*, **30**, 3972 (1965).

(9) R. J. Mohrbacher and N. H. Cromwell, *J. Amer. Chem. Soc.*, **79**, 401 (1957).



elemental analysis, characteristic SO and $SO_2$ peaks in the ir, and their unique nmr spectra. Furthermore, the oxidation of sulfoxide **12** to sulfone **13** link these systems structurally.

When sulfoxide **12** was refluxed in benzene with a small amount of *p*-toluenesulfonic acid for 7 hr, 1-chloronaphthalene was isolated in 20% yield as the only identifiable product. An attractive explanation for the origin of 1-chloronaphthalene involves dehydration of **12** to 2-chloro-1-benzothiepin 1-oxide (**14**) which, after valence bond tautomerism to **16**, undergoes SO elimination. Thiirane 1-oxides[10] are known to thermally extrude SO, as are other heterocyclic systems;[11,12] however, of the thiepin sulfoxides known, thieno[3,4-*d*]thiepin 6-oxide[13] appears to be unstable (however, no mention of SO elimination) while dibenzo-[*b*,*f*]thiepin 5-oxide and its derivatives[14] did not extrude SO. Conversion of a dibenzothiazepinium salt to a phenanthridizinium salt by action of hydrogen peroxide has been explained by sulfoxide formation followed by SO extrusion.[15] An alternative pathway to 1-chloronaphthalene may involve disproportionation of **14** to 2-chloro-1-benzothiepin (known to extrude sulfur readily[16]) and 2-chloro-1-benzothiepin 1,1-dioxide (**15**); however, the absence of **15** in the product mixture precludes this pathway. The chemistry of thiepin sulfoxides is under investigation.

Sulfone **13** requires 92% phosphoric acid at 120–140° for 1 hr in order for dehydration to occur, giving the stable 2-chloro-1-benzothiepin 1,1-dioxide (**15**). The ir spectrum of **15** showed the absence of the hydroxyl group and the presence of the sulfone function, while the uv spectrum of **15** [$\lambda_{max}$ 293 mμ (log ε 4.00), 239 (4.10)] was similar to that of 1-benzothiepin 1,1-dioxide [$\lambda_{max}$ 290 mμ (log ε 3.99), 234 (4.13)].[17] The strong absorption of 1-benzothiepin 1,1-dioxide at 234 mμ was attributed to the new conjugated system[17] which resembled 3-benzothiepin 3,3-dioxide [$\lambda_{max}$ 232 mμ (log ε 4.5)][18] and the absorption maximum for **15** at 239 mμ exhibited the expected bathochromic shift. The nmr spectrum of **15** in $CDCl_3$ had no peaks at higher field than τ 3.46 and showed the expected spin–spin coupling for the $C_3$, $C_4$, and $C_5$ protons. These data are all consistent with the structural assignment for **15**.

A comparison of the acid-catalyzed dehydration of **1**, **12**, and **13** illustrates the influence of the electron-withdrawing sulfoxide and sulfone group, as described above, which lead to normal dehydration and no carbon skeleton rearrangement.

## Experimental Section[19]

*o*-(**Methylthio**)**benzoic Acid** (**5**).—In a modification of the procedure of Kucsman and Kremmer[20] a mixture of dimethyl sulfate (227 g, 1.80 mol) and a solution of thiosalicyclic acid (180 g, 1.17 mol) and sodium hydroxide (95.5 g, 2.39 mol) in water (720 ml) was refluxed for 6 hr and treated with sodium hydroxide (36 g, 0.90 mol) in water (100 ml) and upon work-up gave 189 g (96%) of *o*-(methylthio)benzoic acid, mp 167–169° (lit.[20] mp 170°). Recrystallization from toluene gave white needles, mp 170°.

*o*-(**Methylthio**)**benzyl Alcohol** (**6**).—The method of Grice and Owen[21] was applied to the reduction of *o*-(methylthio)benzoic acid (75.0 g, 0.446 mol) by $LiAlH_4$ (slurry, 17.0 g, 0.446 mol) in ether (500 ml). After 20 hr of reflux and an alkaline work-up, the yield of *o*-(methylthio)benzyl alcohol, bp 114° (0.7 mm), was 59 g (86%). An analytical sample, bp 155–156° (17 mm), $n^{20}D$ 1.6075 [lit.[21] bp 88° (0.001 mm), $n^{20}D$ 1.6060], was obtained after two distillations.

*Anal.* Calcd for $C_8H_{10}OS$: C, 62.30; H, 6.54. Found: C, 62.46, 62.28; H, 6.46, 6.66.

*o*-(**Methylthio**)**benzaldehyde** (**7**). **Method A.**—By application of the procedure of Pratt and van de Castle,[3] freshly prepared manganese dioxide[22] (158 g, 1.82 mol) and *o*-(methylthio)-benzyl alcohol (70.0 g, 0.455 mol) gave after distillation 56.5 g (82%) of *o*-(methylthio)benzaldehyde, bp 97–101° (0.7 mm), $n^{20}D$ 1.6338 [lit.[23] bp 149° (19 mm)]. An analytical sample, bp 80° (0.05 mm), $n^{20}D$ 1.6355, was prepared *via* the bisulfite addition product followed by distillation.

*Anal.* Calcd for $C_8H_8OS$: C, 63.13; H, 5.30. Found: C, 63.42; H, 5.31.

**Method B.**—*o*-(Methylthio)benzyl alcohol (10.6 g, 0.070 mol) in pyridine (25 ml) was oxidized by bispyridine–chromium trioxide (33.7 g, 0.213 mol) in dry pyridine (100 ml) using Holum's[4] procedure and gave 5.7 g (54%) of *o*-(methylthio)benzaldehyde, bp 119–122° (3.8 mm), $n^{20}D$ 1.6308.

*trans-o*-(**Methylthio**)**cinnamic Acid** (**8**).—*o*-(Methylthio)benzaldehyde (12.9 g, 0.085 mol), malonic acid (19.4 g, 0.186 mol), piperidine (0.75 ml), and pyridine (30 ml) were heated in an oil bath at 80° for 1 hr, after which the temperature was increased to 100° for 2 hr and the solution was finally refluxed for 0.5 hr.[5] The solution was cooled, poured onto 12% hydrochloric acid and ice, filtered, and washed with water. The dry solid was recrystallized from toluene and gave 14.8 g (90%) of *trans-o*-(methylthio)cinnamic acid, mp 175–176° (lit.[24] mp 176°).

**Methyl** *trans-o*-(**Methylthio**)**cinnamate** (**9**).—A solution of *trans-o*-(methylthio)cinnamic acid (14.8 g, 0.076 mol) in methanol (160 ml) and concentrated sulfuric acid (6 ml) was refluxed for 6 hr. After the solution was concentrated, diluted with water, and extracted with ether, the ether extract was washed with $NaHCO_3$ solution and water, dried ($MgSO_4$), and distilled. The ester was collected as a light green oil, bp 119–123° (0.5 mm), yield 14.0 g (89%), which crystallized on standing. Two recrystallizations from Skelly B gave pure methyl *trans-o*-(methylthio)cinnamate: mp 43–44°; nmr ($CCl_4$) τ 1.93 (d, 1, $J$ = 15 Hz, Ar**H**C=CHCO$_2$CH$_3$), 2.80 (m, 4, aromatic H), 3.74 (d, 1, $J$ = 15 Hz, ArHC=C**H**CO$_2$CH$_3$), 6.18 (s, 3, OCH$_3$), 7.64 (s, 3, SCH$_3$).

(10) G. E. Hartzell and J. N. Paige, *J. Amer. Chem. Soc.*, **88**, 2616 (1966).
(11) H. H. Szmant and L. M. Alfonso, *ibid.*, **79**, 205 (1957).
(12) R. H. B. Galt, J. D. Loudon, and A. D. B. Sloan, *J. Chem. Soc.*, 1588 (1958).
(13) R. H. Schlessinger and G. S. Ponticello, *Tetrahedron Lett.*, 3017 (1968).
(14) A. Trifunac and E. T. Kaiser, *J. Phys. Chem.*, **74**, 2236 (1970).
(15) C. K. Bradsher and J. W. McDonald, *J. Org. Chem.*, **27**, 4475 (1962).
(16) V. J. Traynelis, J. R. Livingston, and Y. Yoshikawa, unpublished observations.
(17) V. J. Traynelis and R. F. Love, *J. Org. Chem.*, **26**, 2728 (1961).
(18) W. E. Truce and F. J. Lotspeich, *J. Amer. Chem. Soc.*, **78**, 848 (1956).

(19) All melting points and boiling points are uncorrected. Elemental analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind., or Schwartzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were determined on a Perkin-Elmer Infracord, ultraviolet spectra were measured on a Bausch and Lomb Spectronic 505 spectrometer, and the nmr spectra were obtained on a Varian Associates 60-MHz nmr spectrometer.
(20) A. Kucsman and T. Kremmer, *Acta Chim. Acad. Sci. Hung.*, **34**, 75 (1962).
(21) R. Grice and L. Owen, *J. Chem. Soc.*, 1947 (1963).
(22) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *ibid.*, 1094 (1952).
(23) B. Eistert, W. Schade, and H. Selzer, *Chem. Ber.*, **97**, 1470 (1964).
(24) C. Chmelewsky and P. Friedlander, *ibid.*, **46**, 1903 (1913).

*Anal.* Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.83, 63.62; H, 5.93, 5.78.

*trans*-2-(2-Methylthiophenyl)cyclopropanecarboxylic Acid (10). —Trimethyloxosulfonium iodide (14.1 g, 0.064 mol) was added to a stirred slurry of sodium hydride (0.064 mol) in dimethyl sulfoxide (50 ml) under nitrogen and stirred for 15 min. Methyl *trans*-*o*-(methylthio)cinnamate (12 g, 0.058 mol) in dimethyl sulfoxide (20 ml) was added to this mixture at a temperature below 50° and the resulting mixture was heated for 2.5 hr, poured into water, and extracted with $CHCl_3$. After the $CHCl_3$ extract was washed with $H_2O$ and dried ($MgSO_4$) and the solvent was removed, the residue was distilled and gave 1.5 g of crude ester, bp 131–135° (0.55 mm). The crude ester and potassium hydroxide (1.5 g, 0.038 mol) were dissolved in 50% aqueous methanol and refluxed for 2 hr, after which acidification and filtration gave 1.2 g (10% overall yield) of *trans*-2-(2-methylthiophenyl)cyclopropanecarboxylic acid, mp 111–114°. An analytical sample was prepared by crystallization from benzene–Skelly B and had the following constants: mp 115–116°; uv max (95% $C_2H_5OH$) 252 mμ (log ε 3.94); ir ($CHCl_3$) 1680 $cm^{-1}$ (C=O); nmr ($CF_3CO_2H$) τ 2.88 (m, 4, aromatic H), 7.25 (m, 1), 7.62 (s, 3, $SCH_3$), 8.31 (m, 3).

*Anal.* Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.54; H, 5.82.

Attempted Isomerization of *cis*-2-(2-Methylthiophenyl)cyclopropanecarboxylic Acid (3).—A solution of *cis*-2-(2-methylthiophenyl)cyclopropanecarboxylic acid[1a] (100 mg, 0.56 mmol) in 20 ml of 0.1 *N* potassium *tert*-butoxide in *tert*-butyl alcohol was refluxed for 1 week. The solution was acidified, diluted with water, and extracted with $CHCl_3$. When the $CHCl_3$ was removed, 60 mg (60%) of starting acid, mp 166–167° (lit.[1a] mp 168–169°), was recovered.

2-Chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1-Oxide (12). —To a solution of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin (2.38 g, 0.011 mol), prepared as described previously,[1a] and boron trifluoride etherate (2.34 g, 0.011 mol) in anhydrous ether (100 ml) was added a solution of perbenzoic acid (0.15 mol) in anhydrous ether while the temperature was maintained below −10°. After 3 hr at this temperature, the solution was allowed to warm up to room temperature and treated with sodium carbonate solution and the ether layer was separated. The aqueous layer was extracted with $CHCl_3$, the combined $CHCl_3$ and ether solution was dried ($MgSO_4$), and the solvent was removed to give 1.46 g (57%) of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1-oxide as a viscous oil. The oil slowly solidified and crystallization from toluene gave an analytical sample: mp 141–142° dec; uv max (95% $C_2H_5OH$) 255 mμ (log ε 3.53), inflection 230 (3.79); ir (Nujol mull) 3310 (COH) and 1030 $cm^{-1}$ (>S=O); nmr ($CF_3CO_2H$) τ 2.12 (m, 4, aromatic H), 3.37 (d, 1, $J_{C_5-C_{4a}}$ = 6 Hz, $C_5$ H), 3.50 (dd, 1, $J_{C_3-C_{4b}}$ = 6, $J_{C_3-C_{4a}}$ = 3 Hz, $C_3$ H), 6.40 (two dd, 1, $J_{C_{4a}-C_{4b}}$ = 20, $J_{C_{4a}-C_5}$ = 6, $J_{C_{4a}-C_3}$ = 3 Hz, $C_{4a}$ H), 7.28 (dd, 1, $J_{C_{4b}-C_{4a}}$ = 20, $J_{C_{4b}-C_3}$ = 6 Hz, $C_{4b}$ H).

*Anal.* Calcd for $C_{10}H_9ClO_2S$: C, 52.52; H, 3.97. Found: C, 52.74; H, 3.80.

2-Chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1,1-Dioxide (13). Method A.—A solution of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin (4.24 g, 0.020 mol), perbenzoic acid (0.044 mol), and boron trifluoride etherate (6 ml) in ether (130 ml) was allowed to stand overnight, the ether was removed, and the residue was treated with 10% sodium hydroxide solution. The resulting precipitate was filtered, dried, and recrystallized from benzene–hexane (after Norit treatment) to give 3.2 g (70%) of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1,1-dioxide: mp 117.5–119°; uv max (95% $C_2H_5OH$) 237 mμ (log ε 3.74), 270 (3.74), 278 (3.71); ir (Nujol mull) 3310 (COH) and 1320, 1170 $cm^{-1}$ (>S(O)O); nmr ($CDCl_3$) τ 2.2 (m, 4, aromatic H), 3.62 (dd, 1, $J_{5-4a}$ = 6, $J_{5-4b}$ = 4.5 Hz, $C_5$ H), 3.88 (dd, 1, $J_{3-4a}$ = 4.5, $J_{3-4b}$ = 11.5 Hz, $C_3$ H), 6.61 (s, 1, OH), 6.94 (two dd, 1, $J_{4a-4b}$ = 20, $J_{4a-5}$ = 6, $J_{4a-3}$ = 4.5 Hz, $C_{4a}$ H), 7.61 (two dd, 1, $J_{4a-4b}$ = 20, $J_{4b-5}$ = 4.5, $J_{4b-3}$ = 11.5 Hz, $C_{4b}$ H).

*Anal.* Calcd for $C_{10}H_9ClO_3S$: C, 49.09; H, 3.71. Found: C, 49.66; H, 3.85.

Method B.—A solution of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1-oxide (500 mg, 2.2 mmol), 30% hydrogen peroxide (2.5 ml), and acetone (10 ml) was refluxed for 3.5 hr, diluted with water, and extracted with ether. After the ether extract was dried and the solvent was removed, the residue was crystallized from benzene and gave 130 mg (28%) of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1,1-dioxide, mp 110–116°. Recrystallization from benzene–hexane gave pure sulfone, mp 116–117°.

2-Chloro-1-benzothiepin 1,1-Dioxide (15).—2-Chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1,1-dioxide (1.00 g, 0.0041 mol) was added to 92% phosphoric acid prepared by dissolving phosphorus pentoxide (5.0 g) in 85% phosphoric acid (20 ml) and the solution was heated on a steam bath for 30 min and then at 115–143° for 60 min. The reaction mixture was poured onto ice and the solid was filtered and dried to give 0.50 g (54%) of 2-chloro-1-benzothiepin 1,1-dioxide, mp 136–136.5°. Recrystallization from benzene gave an analytical sample: mp 137–138°; uv inflection (95% $C_2H_5OH$) 223 mμ (log ε 4.38), 239 (4.10); uv max 293 mμ (log ε 4.00); ir (Nujol mull) 1310 and 1030 $cm^{-1}$ (>S(O)O); nmr ($CF_3CO_2H$) τ 1.80 (m, 1, $ArC_9$ H), 2.27 (m, 3, ArH), 2.44 (d, 1, $J$ = 12.5 Hz, $C_5$ H), 2.83 (d, 1, $J$ = 7.5 Hz, $C_3$ H), 3.29 (dd, 1, $J_{C_4-C_3}$ = 7.5, $J_{C_4-C_5}$ = 12.5 Hz, $C_4$ H).

*Anal.* Calcd for $C_{10}H_7ClO_2S$: C, 52.98; H, 3.11. Found: C, 53.24; H, 3.13.

Reaction of 2-Chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1-Oxide and Acid.—A mixture of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1-oxide (1.00 g, 0.0044 mol), a few crystals of *p*-toluenesulfonic acid monohydrate, and benzene (50 ml) was refluxed for 7 hr under nitrogen. The solution was cooled and concentrated and the residue was poured onto a column of silica gel (50 g). Elution with Skelly B gave 0.14 g (20%) of 1-chloronaphthalene in fractions 2 and 3. The infrared spectrum of this sample was identical with that of an authentic sample and a mixture melting point of the picrate, mp 129–131°, of the reaction product 1-chloronaphthalene and an authentic sample was not depressed.

Attempted dehydration of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin 1-oxide with phosphorus pentoxide in benzene gave only recovered starting material (80%).

**Registry No.**—**6**, 33384-77-9; **7**, 7022-45-9; **9**, 36287-17-9; **10**, 36287-18-0; **12**, 36287-19-1; **13**, 36287-20-4; **15**, 36287-21-5.