ether solution was dried over magnesium sulfate and the ether removed. A white crystalline residue remained which was diluted to 5.0 ml with CCl_4 and analyzed by ir for unreacted diaziridinone. Comparison of the infrared spectrum to a standard solution revealed that less than 4% of the diaziridinone had been destroyed; a band at 1665 cm^{-1} of very low intensity indicated the formation of the urea.

A solution of sodium naphthalenide (2.1 mmol in 10.0 ml of THF) was treated with 0.297 g (0.99 mmol) of the diaziridinone under the same conditions as before affording 0.230 g of 1,3-bis-(1,1-dimethyl-2-phenylethyl)urea, mp 180–182°, mmp 180–182°, and identical in infrared spectrum with an authentic sample.

Registry No.—**1a,** 19656-74-7; 1,3-di-*tert*-butylurea, 5336-24-3; *tert*-butyllithium, 594-19-4; sodium naphthalenide, 3481-12-7; bis(1,1-dimethyl-2-phenylethyl)-diaziridinone, 19694-14-5.

Acknowledgment.—We wish to thank C. S. Hutchins for the attempted reduction of the α-lactam, **8.**

Seven-Membered Heterocycles. V. Synthesis and Structure of Halogenated 3,4-Dihydro-1-benzothiepin-5(2*H*)-ones[1a,b]

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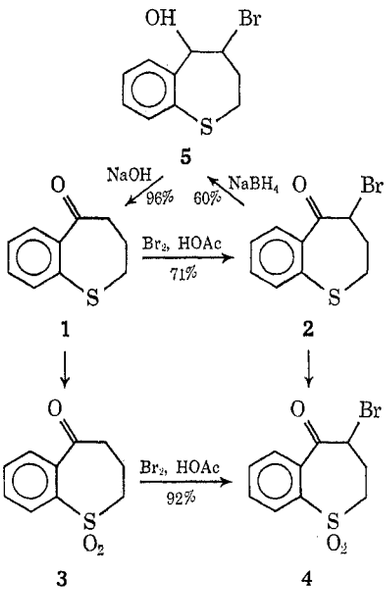
Bromination of 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**1**) gave 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**), which was reduced to the bromohydrin **5**. Treatment of **5** with base regenerated the starting ketone **1**. Chlorination of **1** with *N*-chlorosuccinimide (NCS) or sulfuryl chloride produced exclusively *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**6**). *trans*-2,4-Dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**7**) was available by the stereoselective ring-opening addition of HCl on 8-chlorocyclopropa[*b*][1]benzothiopyran-7-one (**8**). In contrast the reaction of **2** with sulfuryl chloride or NCS provided a mixture of *cis*- (**11**) and *trans*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**12**) in which the trans isomer was highly predominant. Nucleophilic displacement reactions were used to convert **2** to 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**17**) and 4-iodo-3,4-dihydro-1-benzothiepin-5(2*H*)-one. Sulfones of the above halo ketones were also prepared either by oxidation of the corresponding sulfides or halogenation of keto sulfones. The structural and stereochemical assignments for these compounds were made from interpretation of ir and nmr spectra. The mechanism offered for the stereoselective chlorination of **1** to give *cis*-**6** entailed first C_2 chlorination followed by C_4 substitution *via* a transannular chlorination in the chlorosulfonium ion **19** intermediate. Formation of predominantly trans **12** in the sulfuryl chloride reaction with **2** is rationalized by the usual ion pair intermediate **21** proposed for α-chlorination of sulfides by sulfuryl chloride.

Halogenated 3,4-dihydro-1-benzothiepin-5(2*H*)-ones can serve as potential intermediates for introducing unsaturation into the thiepin ring and thus providing precursors for the synthesis of 1-benzothiepin derivatives. In this paper we emphasize the synthesis and structural assignments for a variety of halogenated 3,4-dihydro-1-benzothiepin-5(2*H*)-ones and in the subsequent report[2] concentrate on the reactions of these halo ketones with base.

Bromination of 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**1**) proceeded readily to form the 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**),[3] which was characterized as the corresponding sulfone **4** also available by direct bromination of **3**. The position of bromination was established by reduction of **2** to the bromohydrin **5**, which undergoes base-catalyzed elimination of HBr to form the starting ketone **1**. An infrared study of the carbonyl frequencies for ketones **1** and **2** (see Table I) showed a band displacement of 15 cm^{-1} to higher frequency for the bromo ketone **2**, thus favoring the conformation which places the bromine atom in a quasi-equatorial position[4] and puckers the C_2 and C_3 carbons out of the plane of the ring. The absence of any appreciable bathochromic shift in the uv spectra of **1** and **2** is also consistent with the quasiequatorial assignment



(1) (a) For part IV in this series see V. J. Traynelis and D. M. Borgnaes, *J. Org. Chem.*, **37**, 3824 (1972). (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (c) Abstracted from a portion of the Ph.D. Dissertation submitted by J. C. S. in Dec 1971 and Y. Y. in May 1973 at West Virginia University. (d) Abstracts from a portion of the Ph.D. Dissertation submitted by R. F. L. in June 1960 and D. M. B. in Aug 1968 at the University of Notre Dame.

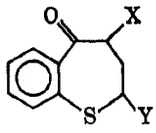
(2) V. J. Traynelis, J. C. Sih, and D. M. Borgnaes, *J. Org. Chem.*, **38**, 2629 (1973).

(3) K. Sindelar and M. Protiva, *Collect. Czech. Chem. Commun.*, **33**, 4315 (1968).

(4) R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Amer. Chem. Soc.*, **74**, 2828 (1952); E. J. Corey, *ibid.*, **75**, 2301 (1953); N. L. Allinger and J. Allinger, *ibid.*, **80**, 5476 (1958).

TABLE I

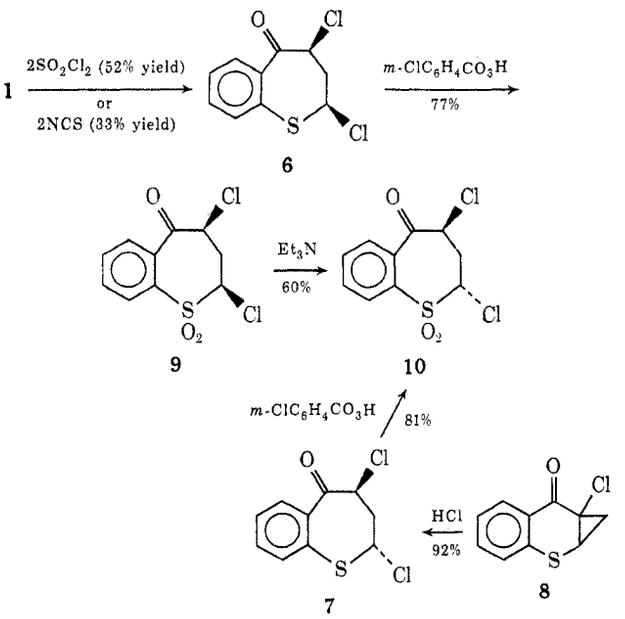
UV AND IR SPECTRAL DATA FOR KETONE 1 AND ITS HALOGENATED DERIVATIVES



Compd	95% EtOH λ_{max}, nm ($\epsilon \times 10^{-3}$)	95% EtOH Δ, nm	CCl_4 soln >C=O, cm^{-1}	CCl_4 soln Δ, cm^{-1}	$CHCl_3$ soln >C=O, cm^{-1}	$CHCl_3$ soln Δ, cm^{-1}
X = Y = H (1)	241 (18.3)		1680		1675	
X = Br; Y = H (2)	243 (17.6)	2	1695	15	1690	15
X = Cl; Y = H (15)					1690	15
cis, X = Y = Cl (6)			1710	30	1700	25
trans, X = Y = Cl (7)			1700	20	1690	15
cis, X = Br; Y = Cl (11)			1705	25	1695	20
trans, X = Br; Y = Cl (12)			1700	20	1695	20

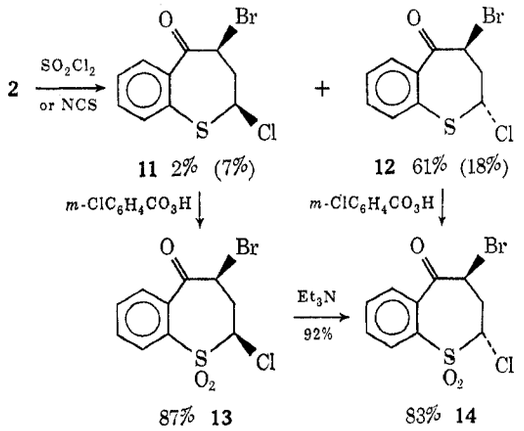
for bromine.[5] Such a geometry for **2** favors an axial approach of the borohydride ion from the side opposite the bromine. Therefore, the resulting bromohydrin most likely has the hydroxyl and bromine cis, which permits a facile trans elimination of hydrogen bromide to regenerate ketone **1**.

The reaction of simple sulfides with sulfuryl chloride[6] or *N*-chlorosuccinimide (NCS)[7] readily forms α-chloro sulfides. In addition sulfuryl chloride is known to react with ketones to give α-chloro ketones.[8] When 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**1**) was allowed to react with sulfuryl chloride or NCS, the only stable crystalline product isolated was *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**6**). The yield of **6** was improved with the use of 2+ equiv of chlorinating agent and only the cis isomer was formed. A spectroscopic study of the reaction mixture failed to detect any of the trans isomer. *trans*-3,4-Dihydro-1-benzothiepin-5(2*H*)-one (**7**) was obtained by a stereoselective ring-opening addition of hydrogen chloride to 7a-chloro-



cyclopropa[*b*][1]benzothiopyran-7-one (**8**).[9] The dichloro ketones were characterized by conversion to their corresponding sulfones **9** and **10**. The cis dichloro keto sulfone **9** was readily isomerized by weak base to the more stable trans compound **10**.

A different stereochemical outcome results in the chlorination of 4-bromo-3,4-dihydro-1-benzothiepin-5-(2*H*)-one (**2**) with either sulfuryl chloride or NCS. Both *cis*- and *trans*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**11** and **12**, respectively) were isolated with the trans isomer highly predominant. Again oxidations to the corresponding sulfones **13** and **14** were readily accomplished with *m*-chloroperbenzoic



acid and the conversion of the cis halo sulfone **13** to the more stable trans isomer **14** occurred rapidly with triethylamine.

Inspection of the data in Tables I and II, particularly the nmr data, reveals marked spectral similarities between the cis dihalo ketones **6** and **11** and between the trans dihalo ketones **7** and **12**. Displacement of the carbonyl stretching frequency to higher values (see Table I) for all the dihalogenated ketones supports a quasiequatorial location for the C_4 halogen. However, the magnitude of the carbonyl band displacement appears larger than expected and may be rationalized by bending the carbonyl group out of the plane of the benzene ring. Additional support for the nonplanar relationship of the carbonyl group and the benzene ring is found in the reduced deshielding effect of the car-

(5) R. C. Cookson, *J. Chem. Soc.*, 282 (1954); E. J. Corey and H. J. Burke, *J. Amer. Chem. Soc.*, **77**, 5418 (1955); A. Hassner and N. H. Cromwell, *ibid.*, **80**, 893 (1958).

(6) F. G. Bordwell and B. M. Pitts, *ibid.*, **77**, 572 (1955); L. A. Paquette, and L. S. Wittenbrook, *ibid.*, **90**, 6790 (1968).

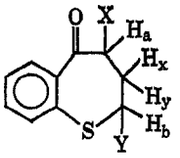
(7) D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969), and earlier papers.

(8) D. P. Wyman and P. R. Kaufman, *ibid.*, **29**, 1956 (1964).

(9) The preparation of this compound is described in ref 2.

TABLE II

NMR SPECTRAL DATA FOR 2,4-DIHALO-3,4-DIHYDRO-1-BENZOTHIEPIN-5(2*H*)-ONES



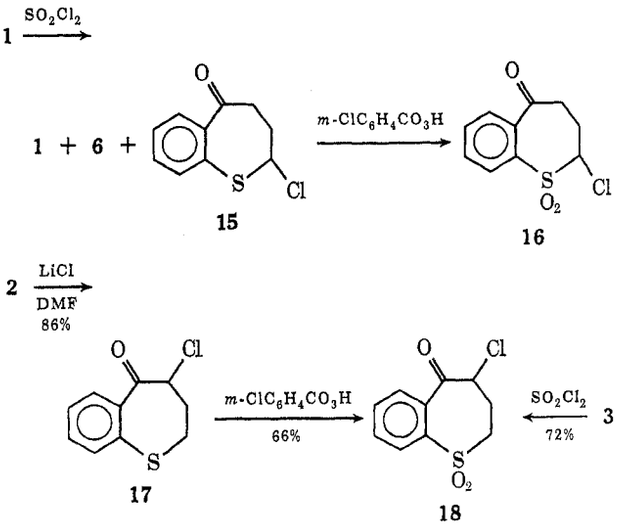
Compd	C_4 H$_a$[a]	J_{ax}[b]	J_{ay}[b]	C_2 H$_b$[a]	J_{bx}[b]	J_{by}[b]	C_3 H$_x$[a]	J_{xy}[b]	C_3 H$_y$[a]
cis, X = Y = Cl (6)	5.55 (t)	7	7	4.95 (dd)[c]	4.3	11.2	3.24 (two dd)[d]	14	2.63 (two dd)
trans, X = Y = Cl (7)	5.29 (dd)	7.5	7	5.09 (dd)	7	7	2.98 (dd)	0	2.98 (dd)
cis, X = Br; Y = Cl (11)	5.37 (dd)	6	8	4.72 (dd)	4	12	3.18 (two dd)	14	2.57 (two dd)
trans, X = Br; Y = Cl (12)	5.25 (dd)	6.5	8.5	5.02 (dd)	6.5	5.5	2.96 (dd)	0	2.92 (dd)

[a] Chemical shifts are in parts per million. [b] Coupling constants are in hertz. [c] A doublet of doublets. [d] Eight lines, two doublet of doublets.

bonyl group on the C_6 H.[10] A study of the solvent effect on the nmr resonance of the C_4 H of the dihalo ketones **6**, **11**, and **12** showed solvent shifts ($\Delta_{C_6H_6}^{CHCl_3} = \delta_{CHCl_3} - \delta_{C_6H_6}$) of +1.05, +0.40, and +0.25. These values, interpreted according to Bhacca and Williams,[11] lend further support to the quasiequatorial assignment for the C_4 halogens.

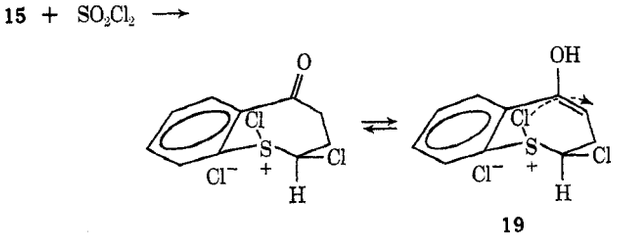
Cis and trans configurational assignments for the dihalogenated ketones were initially made on the basis of the coupling constants between the C_4 H and C_3 H's and the C_2 H and C_3 H's (see Table II). An examination of Dreiding models of the trans dihalo ketones **7** and **12** shows that the C_4 H and the C_2 H have a similar dihedral angular relationship with each of the C_3 H's and thus the coupling constants are comparable. However, with the cis dihalo ketones **6** and **11** the C_2 H has a markedly different angular relationship with each of the C_3 H's and therefore one observes considerable differences in the coupling constants between C_2 H and the C_3 H's as well as differences from the C_4 H and C_3 H's coupling constants.

The stereoselective dichlorination of **1** to give only *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**6**) in contrast to the chlorination of **2** to give predominantly *trans*-2-chloro-4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**12**) merits explanation. A study of the chlorination of **1**, where sulfuryl chloride was added in half-mole increments until a total of 2 mol was introduced, revealed that chlorination occurred at the C_2 position first and subsequent chlorination went to C_4. However, even with limited quantities of sulfuryl chloride (after the first 0.5 mol) some dichloro ketone **6** was formed. Since 2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**15**) appeared to be thermally sensitive, the reaction mixture was oxidized with *m*-chloroperbenzoic acid and **15** was converted to the stable sulfone **16**. Sulfone **16** differed in physical and spectral properties from 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**18**), which was prepared as shown below. Chlorination of keto sulfone **3** should proceed into the C_4 position, since sulfones are not known to α-chlorinate with sulfuryl chloride. This



position of substitution was confirmed by the alternate synthesis of sulfone **18** from the 4-bromo ketone **2** *via* 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**17**).

The conversion of **1** to **6** *via* sulfuryl chloride or NCS requires C_2 substitution first followed by C_4-chlorination, with the stereochemical control exercised in the second step. If the C_4-chlorination proceeded *via* intermolecular attack by sulfuryl chloride or Cl^+ on the enol of **15**,[8] one would expect to obtain a mixture of *cis*- and *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-ones (**6** and **7**, respectively).[12] A more likely alternative for conversion of **15** to **6** involves formation of the chlorosulfonium salt **19**, which under-



goes a transannular transfer of Cl^+ from sulfur to the C_4 position.[13] Such chlorosulfonium salts form rapidly

(10) R. H. Martin, N. Defay, and F. Gaerts-Evrard, *Tetrahedron*, **20**, 1505 (1964). Deshielding effects of the carbonyl group in tetralone on the C_8 H (ortho to the carbonyl) causes the C_8 H to be displaced approximately 0.7 ppm downfield from the remainder of the aromatic hydrogens. This difference between the ortho hydrogen and the other aromatic hydrogens in 2,3-benzocyclohept-2-enone is reduced to 0.4 ppm. In the bromo chloro ketones **11** and **12** the ortho hydrogen (C_8 H) is not displaced appreciably and simply merges with the absorption of the other aromatic hydrogens.

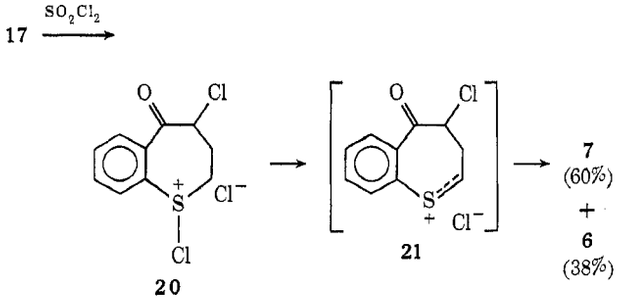
(11) D. H. Williams, and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965); *Tetrahedron Lett.*, 3127 (1964).

(12) In equilibration experiments of **6** and **7** *via* their common enol, one finds approximately equal amounts of each ketone; see ref 2.

(13) Since the reaction of sulfides and sulfuryl chloride generates HCl, the most likely sulfonium salt intermediate involved in Cl^+ transfer is the enol form **19**.

in the reaction of sulfides with sulfuryl chloride[14] and are proposed intermediates in the α-chlorination of sulfides.[7] Chlorosulfonium ion **19** exhibits a conformation which places the SCl near the C_4 position while the C_2 chlorine occupies an equatorial-like position. Thus transannular chlorination from this conformation would lead stereoselectively to the cis isomer **6**. When chlorosulfonium salt formation is precluded as with sulfones, the reaction of **16** and sulfuryl chloride produced exclusively the more stable trans dichloro sulfone **10**.

Further support for the C_2, C_4 dichlorination sequence in the conversion of **1** to **6** is available from the reaction of 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**17**) with sulfuryl chloride. The products from this reaction were trans (**7**) (60%) and cis isomer (**6**) (38%) in a ratio similar to an equilibrium mixture.[12] The initial chlorosulfonium ion **20** forms the ion pair intermediate[7] **21**, which lacks stereochemical control



and leads to the product mixture **6** and **7**. The markedly different stereochemical outcome of the reaction of **17** and sulfuryl chloride excludes **17** as an intermediate in the formation of **6** from **1**.

The reaction of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**) with sulfuryl chloride introduces the C_2 chlorine in a pathway analogous to reaction of **17** and sulfuryl chloride. Therefore the stereochemical outcome in the chlorination of **2** which forms predominantly the trans isomer **12** probably reflects the greater stability of trans (**12**) over cis isomer (**11**).

4-Iodo-3,4-dihydro-1-benzothiepin-5(2*H*)-one was readily available from the bromo ketone **2** and potassium iodide in acetone.

Experimental Section[15]

4-Bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (2).—A solution of bromine (16 g, 0.10 mol) in acetic acid (30 ml) was slowly added to a stirred solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one[16] (**1**) (20 g, 0.112 mol) in acetic acid (50 ml). The reaction mixture was stirred for 2 hr and poured into 400 ml of H_2O containing $NaHSO_3$ (0.5 g), and the solid which separated was filtered and crystallized from methanol to give 19.6 g (71%) of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**), mp 87–89°. Recrystallization from ethanol and cyclohexane gave an analytical sample: mp 89–90° (lit.[3] mp 86.5–87°); uv max (95% C_2H_5OH) 243 nm (log ε 4.24), 261 (3.79), 330 (3.55); ir ($CHCl_3$) 1694 cm^{-1} (>C=O); nmr ($CDCl_3$) δ 7.84 (m, 1, C_9 H), 7.36 (m, 3, C_6, C_7, C_8 H's), 5.35 (m, 1, $-SCH_2CH_2CHBr$), 2.40–3.47 (m, 4, $-SCH_2CH_2-$).

Anal. Calcd for $C_{10}H_9BrOS$: C, 46.70; H, 3.53. Found: C, 46.84; H, 3.68.

4-Bromo-5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin (5).—A solution of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**) (5.00 g, 0.019 mol) in 95% ethanol (15 ml) was added over 1 hr to a stirred slurry of sodium borohydride (0.36 g, 0.009 mol) in 60% ethanol (10 ml), and the mixture was refluxed for an additional 1 hr. After the solution was poured onto crushed ice and hydrochloric acid, the resulting solid was filtered, dried, and recrystallized from Skelly B to give 2.9 g (60%) of 4-bromo-5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin (**5**): mp 93–94°; ir (KBr) 3410 cm^{-1} (strong, broad, $^-$OH); nmr ($CDCl_3$) δ 7.27 (m, 4, aromatic H's), 5.36 (s, 1, OH), 4.61 (m, 1, $-CHBrCH-OH-$), 2.2–2.9 (m, 5, $-SCH_2CH_2CHBr$).

Anal. Calcd for $C_{10}H_{11}BrOS$: C, 46.33; H, 4.25; Br, 30.89. Found: C, 46.58; H, 4.30; Br, 30.80.

Reaction of 4-Bromo-5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin with Sodium Hydroxide.—After a mixture of 4-bromo-5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin (**5**) (580 mg, 2.30 mmol), sodium hydroxide (94 mg, 2.3 mmol), and water (20 ml) was stirred at room temperature for 80 min, the solution was neutralized with HCl and extracted with $CHCl_3$ (2 × 20 ml) and the $CHCl_3$ extract was washed with water and dried (Na_2SO_4). Removal of the solvent under vacuum gave 380 mg (96%) of 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**1**) which had an infrared spectrum identical with that of an authentic sample.

4-Bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-Dioxide (4). Method A.—Bromine (16.0 g, 0.10 mol) was added over a period of 30 min to a solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide[16] (**3**) (21.0 g, 0.10 mol) in glacial acetic acid (200 ml) maintained at 60°. The reaction mixture was kept at 60° for an additional 1 hr, cooled to room temperature, and poured into 1 l. of ice water and the solid which separated was filtered and dried. Recrystallization of the solid from acetone afforded 26.8 g (92%) of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**4**): mp 156–157° (lit.[3] mp 143.5–144°); uv max (95% C_2H_5OH) 224 nm (log ε 3.59), 242 (3.56), 270 (3.29), 308 (2.64); ir ($CHCl_3$) 1702 (>C=O), 1335, 1310, 1160, 1110 cm^{-1} ($>SO_2$); nmr (CD_3COCD_3) δ 8.05 (m, 1, C_9H), 7.87–7.46 (m, 3, C_6, C_7, C_8 H's), 5.05 (dd, J = 3, 6 Hz, 1, $SO_2CH_2CH_2CHBr$), 3.90–3.58 (m, 2, $-SO_2CH_2-$), 3.40–2.45 (m, 2, $-SO_2CH_2CH_2CHBr-$).

Anal. Calcd for $C_{10}H_9BrO_3S$: C, 41.54; H, 3.14. Found: C, 41.82; H, 3.40.

Method B.—A solution of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**) (1.0 g, 3.9 mmol), glacial acetic acid (10 ml) and 30% hydrogen peroxide (3 ml) was allowed to stand overnight, poured into water (50 ml) and the precipitate filtered and dried. Recrystallization of this solid from acetone gave 0.35 g (39%) of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide, mp 156–157°.

***cis*-2,4-Dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (6). Method A.**—After a mixture of 3,4-dihydro-1-benzothiepin-5(2*H*)-one[16] (**1**) (4.00 g, 22.5 mmol), *N*-chlorosuccinimide (6.14 g, 46.0 mmol), and CCl_4 (30 ml) was stirred at room temperature for 16 hr, the succinimide was filtered, and evaporation of the solvent under vacuum gave a pale yellow solid. Recrystallization of this solid from hexane–$CHCl_3$ afforded 1.80 g (33%) of *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**6**), as a white, crystalline solid: mp 108–109°; ir (KBr) 1695 cm^{-1} (>C=O); nmr ($CDCl_3$) δ 7.33–8.00 (m, 4, aromatic H's), 5.55 (t, $J_{C_4-C_{3x}} = J_{C_4-C_{3y}}$ = 7 Hz, 1, O=CCHCl), 4.95 (dd, $J_{C_2-C_{3x}}$ = 11.2, $J_{C_2-C_{3y}}$ = 4.3 Hz, 1, –SCHCl), 3.24 (two dd, $J_{C_{3x}-C_{3y}}$ = 14, $J_{C_{3x}-C_2}$ = 4.5, $J_{C_{3x}-C_4}$ = 7 Hz, 1, $-SCHClCH_xH_yCHCl$), 2.63 (two dd, $J_{C_{3y}-C_{3x}}$ = 14, $J_{C_{3y}-C_2}$ = 11, $J_{C_{3y}-C_4}$ = 7 Hz, 1, $-SCHClCH_xH_yCHCl$).

Anal. Calcd for $C_{10}H_8Cl_2OS$: C, 48.60; H, 3.26; Cl, 28.69. Found: C, 48.66; H, 3.32; Cl, 28.79.

Method B.—Sulfuryl chloride (10.0 ml, 124 mmol) was added dropwise over 30 min to a stirred solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one[16] (**1**) (10.0 g, 56 mmol) in CH_2Cl_2 (100 ml) at room temperature. The reaction mixture was refluxed (opening fitted with a $CaCl_2$ drying tube) for 2 hr, the solvent was removed under vacuum, and the residue was recrystallized from hexane–$CHCl_3$. The yield of *cis*-2,4-dichloro-3,4-dihydro-1-benzothie-

(14) V. J. Traynelis and Y. Yoshikawa, unpublished results. Reaction of sulfides with sulfuryl chloride occurred rapidly at low temperatures to form the chlorosulfonium chloride, which was readily converted to the corresponding sulfoxide or alkoxysulfonium salt.

(15) All melting points and boiling points are uncorrected. Elemental analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind., or Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were determined on a Perkin-Elmer Model 137-B, Model 21, or a Beckman IR-8 spectrophotometer, uv spectra were measured on a Perkin-Elmer Spectracord or a Bausch and Lomb 505 spectrophotometer, and nmr spectra were obtained on a Varian Associates Model HA-60 or Model T-60 spectrometer.

(16) This ketone was prepared as previously described: V. J. Traynelis and R. F. Love, *J. Org. Chem.*, **26**, 2728 (1961).

pin-5(2*H*)-one (**6**), mp 108–109°, was 7.20 g (52%). The ir and nmr spectra and mixture melting point were identical with those of the sample prepared by method A. An nmr spectrum of the crude residue before crystallization showed the absence of the trans dichloro isomer.

cis-2,4-Dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-Dioxide (**9**).—A solution of *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**6**) (1.52 g, 6.16 mmol) in $CHCl_3$ (15 ml) was added dropwise over a 15-min period to a stirred solution of *m*-chloroperbenzoic acid (2.44 g, 14.2 mmol) in $CHCl_3$ (30 ml) maintained at −10 to −15°. After the reaction mixture was allowed to warm to room temperature and remain overnight, the *m*-chlorobenzoic acid was filtered, and the filtrate was washed with Na_2CO_3 (10%) and dried (Na_2SO_4). After the solvent was removed, the white residue was recrystallized from benzene and gave 1.32 g (77%) of *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**9**): mp 172–174° dec; ir (KBr) 1705 (>C=O), 1330, and 1150 cm^{-1} (<SO_2); nmr (CD_3COCD_3) δ 7.65–8.18 (m, 4, aromatic H's), 5.74 (dd, $J_{C_4-C_{3x}} = 5.5$, $J_{C_4-C_{3y}} = 9.5$ Hz, 1, $-CO_2CHCl-$), 5.23 (dd, $J_{C_2-C_{3x}} = 3.5$, $J_{C_2-C_{3y}} = 10.5$ Hz, 1, $-SO_2CHCl-$), 3.37 (two dd, $J_{C_{3x}-C_{3y}} = 14$, $J_{C_{3x}-C_4} = 5.5$, $J_{C_{2y}-C_2} = 3.5$ Hz, 1, $-SO_2CHClCH_xH_yCHCl$), 2.49 (two dd, $J_{C_{3y}-C_{3x}} = 14$, $J_{C_{3y}-C_4} = 9.5$, $J_{C_{3y}-C_2} = 11$ Hz, 1, $-SO_2CHClCH_xH_yCHCl-$).

Anal. Calcd for $C_{10}H_8Cl_2O_3S$: C, 43.03; H, 2.89; O, 17.20. Found: C, 43.21; H, 2.71; O, 17.11.

trans-2,4-Dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**7**).—Hydrogen chloride gas was bubbled into a solution of 7a-chlorocyclopropa[*b*][1]benzothiopyran-7-one[2] (**8**) (2.00 g, 9.50 mmol) in $CHCl_3$ (10 ml) for 20 min at room temperature. The excess HCl gas was removed under a stream of N_2 and evaporation of the solvent gave a white solid, mp 106–109°. An nmr spectrum of this crude product showed the absence of the cis-dichloro isomer **6**. Recrystallization of the crude solid from hexane–$CHCl_3$ afforded 2.15 g (92%) of *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**7**), as long, fluffy needles: mp 108–109°; ir (CCl_4) 1700 cm^{-1} (>C=O); nmr ($CDCl_3$) δ 7.91–7.40 (m, 4, aromatic H's), 5.29 (dd, $J_{C_4-C_{3x}} = 7.5$, $J_{C_4-C_{3y}} = 7$ Hz, 1, $-COCHCl-$), 5.09 (dd, $J_{C_2-C_{3x}} = 7$, $J_{C_2-C_{3y}} = 7$ Hz, 1, $-SCHCl$), 2.98 (t, $J_{C_3-C_4} = 7$, $J_{C_3-C_2} = 7$ Hz, 2, $-SCHClCH_xH_yCHCl$). A mixture melting point of *trans*- and *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one, mp 108–109° for each, was depressed to 81–89°.

Anal. Calcd for $C_{10}H_8Cl_2OS$: C, 48.60; H, 3.26; Cl, 28.69. Found: C, 48.40; H, 3.34; Cl, 28.78.

The same result was obtained when the above reaction was carried out in benzene instead of $CHCl_3$.

A solution of concentrated HCl (5 ml), 7a-chlorocyclopropa[*b*][1]benzothiapyran-7-one[2] (**8**) (1.59 g, 7.60 mmol), dioxane (17 ml), and H_2O (2 ml) was stirred at room temperature for 1 hr and poured onto crushed ice and gave 1.43 g of crude dichloro ketone **7**, mp 103–108°. Recrystallization of the crude solid from hexane–$CHCl_3$ provided 1.25 g (68%) of the trans dichloro ketone **7**, mp 107.5–109°.

trans-2,4-Dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-Dioxide (**10**). **Method A.**—A solution of triethylamine (2.50 ml, 18 mmol), *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**9**) (0.50 g, 1.79 mmol), and $CHCl_3$ (20 ml) was warmed on a steam bath for 1 min and allowed to remain at room temperature for 30 min. The $CHCl_3$ solution was washed with 10% HCl (5 × 15 ml) and washed with H_2O, the organic layer was dried (Na_2SO_4), and the solvent was removed to give a solid, mp 173–177°. Recrystallization of this solid from benzene gave 0.30 g (60%) of *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**10**): mp 178.5–180°; ir (KBr) 1710 (>C=O), 1328 and 1129 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.17 (m, 1, C_9 H), 7.90–7.51 (m, 3, C_6, C_7, C_8 H's), 5.29 (t, $J_{C_4-C_3} = 5.5$ Hz, 1, $-COCHCl$), 5.00 (t, $J_{C_2-C_3} = 5.5$ Hz, 1, $-SO_2CHCl-$), 3.09 (t, $J_{C_3-C_2} = J_{C_3-C_4} = 5.5$ Hz, 2, $-SO_2CHClCH_2CHCl-$). A mixture melting point of the cis and trans dichloro sulfones was depressed, 163–172°.

Anal. Calcd for $C_{10}H_8Cl_2O_3S$: C, 43.03; H, 2.89; Cl, 25.40. Found: C, 42.80; H, 2.79; Cl, 25.19.

Method B.—Using the procedure for the preparation of *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide, the reaction of *m*-chloroperbenzoic acid (0.96 g, 5.59 mmol) and *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**7**) (0.70 g, 2.43 mmol) gave, after recrystallization from benzene, 0.55 g (81%) of *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**10**), mp 179–180°.

Method C.—Sulfuryl chloride (338 mg, 2.5 mmol) in $CHCl_3$ (3 ml) was added dropwise to a stirred solution of 2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**16**) (122 mg, 0.5 mmol) in $CHCl_3$ (6 ml). After the reaction mixture was refluxed for 24 hr, the solvent was removed and the residue was recrystallized from benzene to give 60 mg (43%) of *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**10**), mp 180–182°. The nmr spectrum was identical with that of the above sample and a mixture melting point with the above sample was not depressed.

Nmr analysis of the crude reaction product indicated that *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide was not formed.

Reaction of 3,4-Dihydro-1-benzothiepin-5(2*H*)-one with SO_2Cl_2 (1 Equiv).—After a solution of sulfuryl chloride (2.70 g, 20 mmol) and 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**1**) (3.56 g, 20 mmol) in CH_2Cl_2 (40 ml) was stirred and heated at 50–55° for 3 hr, the solvent was removed under vacuum and gave 4.1 g of a yellow oil. Thin layer chromatography of the crude oil on silica G_{254} using benzene–ethanol (12:3) and hexane–benzene (9:3) as eluents indicated three components in the mixture. Spectral analysis of the crude oil suggested the presence of 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**1**) [ir 1680 cm^{-1} (>C=O), nmr ($CDCl_3$) δ 2.2 ($-SCH_2CH_2CH_2C=O$)], *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**6**) [ir 1690–1700 cm^{-1} (>C=O); nmr ($CDCl_3$) δ 4.87 (dd, J = 4, 11 Hz)], and 2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**15**) (identified below). The absence of *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**7**) in the crude mixture was established by adding a sample of trans dichloro ketone **7** and observing the appearance of new bands for the trans isomer in the nmr spectrum.

A solution of the above crude product mixture (4.1 g) and *m*-chloroperbenzoic acid (8.28 g, 48 mmol) in $CHCl_3$ (45 ml) was allowed to remain at room temperature overnight. After the reaction mixture was filtered, the filtrate washed with Na_2CO_3 solution (10%) and water, and the organic layer dried ($MgSO_4$), the $CHCl_3$ was removed and gave 4.5 g of a solid, mp 97–103°. Fractional crystallization of the crude solid (4.2 g) from $CHCl_3$ and 95% ethanol led to the isolation of 0.52 g (13%) of 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**3**), mp 159.5–160.5° (lit.[16] mp 157–158°), the nmr of which was identical with that of an authentic sample and the mixture melting point was not depressed; 0.22 g (4.3%) of *trans*-2,4-dichloro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**10**), mp 180–183°, the nmr of which was identical with that of an authentic sample and the mixture melting point was not depressed; and 1.64 g (35%)[17] of 2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**16**): mp 149–150°; ir ($CHCl_3$) 1700 (>C=O), 1330, 1280, 1190, 1140, and 1120 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.07 (m, 1, C_9 H), 7.87–7.50 (m, 3, C_6, C_7, C_8 H's), 5.20–4.99 (m, 1, $-SO_2CHCl-$), 3.22–1.87 (m, 4, $-SO_2CHClCH_2CH_2C=O$).

Anal. Calcd for $C_{10}H_9ClO_3S$: C, 49.08; H, 3.71; Cl, 14.49. Found: C, 49.21; H, 3.68; Cl, 14.31.

A second experiment was performed in which sulfuryl chloride was added in increments until 2 equiv was introduced. A solution of sulfuryl chloride (337 mg, 2.5 mmol) in CH_2Cl_2 (3 ml) was added dropwise to a solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**1**) (890 mg, 5 mmol) in CH_2Cl_2 (7 ml) and the reaction was stirred at room temperature for 100 min. After the reaction mixture was dried (Na_2SO_4), the solvent was removed and the residue (943 mg), *via* nmr analysis, contained *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**6**) (3%), 2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**15**) (24%), and 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**1**) (73%).

The above residue in CH_2Cl_2 (7 ml) was treated with sulfuryl chloride (337 mg, 2.5 mmol) in CH_2Cl_2 (3 ml) and the mixture was refluxed for 1 hr. After the solvent was removed, analysis of the residue by its nmr spectrum showed the following compounds: cis-dichloro ketone **6** (17.5%), 2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (45%), and unchlorinated ketone **1** (37.5%).

The preceding residue was mixed with sulfuryl chloride (674 mg, 5 mmol) in CH_2Cl_2 and the mixture was refluxed for 2.5 hr. The solvent was removed and the nmr spectrum of the residue showed a mixture of the cis dichloro ketone **6** (50%), 2-chloro ketone **15** (40%), and unchlorinated ketone **1** (10%).

(17) The per cent yields were calculated from 3,4-dihydro-1-benzothiepin-5(2*H*)-one and are corrected to represent the total sample (4.5 g) isolated in the oxidation reaction.

4-Chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (17).—After a mixture of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**) (7.0 g, 27.2 mmol), lithium chloride (11.5 g, 272 mmol), and dimethylformamide (50 ml) was allowed to stir for 3 days at ambient temperatures, the reaction mixture was poured into 300 ml of water. The resulting precipitate was filtered and dried to give 5.7 g (98%) of 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**17**). Recrystallization of the crude product from ethanol gave 4.99 g (86%) of pure, colorless, crystalline **17**: mp 84.5–85.5°; ir ($CHCl_3$) 1690 cm^{-1} (>C=O); nmr ($CDCl_3$) δ 7.7–8.0 (m, 1, C_9 H), 7.1–7.6 (m, 3, C_6, C_7, C_8 H's), 5.2–5.5 (m, 1, –COCHCl–), 2.2–3.4 (m, 4, $-SCH_2CH_2-$).

Anal. Calcd for $C_{10}H_9ClOS$: C, 56.46; H, 4.27; Cl, 16.67. Found: C, 56.21; H, 4.08; Cl, 16.53.

Reaction of 4-Chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (17) with SO_2Cl_2.—A solution of sulfuryl chloride (1.35 g, 0.01 mol) in methylene chloride (5 ml) was added dropwise to a stirred solution of 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**17**) (2.13 g, 0.01 mol) in methylene chloride (20 ml). After the mixture was refluxed gently for 1 hr, the solvent was removed *in vacuo* and the remaining clean yellow oil (2.4 g, 96% monochlorination) solidified upon standing in the refrigerator. An nmr analysis of the crude product showed the presence of *cis*- and *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one in a ratio of 40:60.[18]

Fractional crystallization of the mixture from $CHCl_3$–hexane led to the separation into the trans isomer **7** (750 mg, 30%, mp 103–105°) and the cis isomer **6** (190 mg, 8%, mp 104–107°). These compounds had nmr spectra identical with those of authentic samples. The combined mother liquor from the fractional crystallization showed the presence of both isomers which could not be separated further.

4-Chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-Dioxide (18). Method A.—Sulfuryl chloride (1.20 ml, 14.7 mmol) in methylene chloride (10 ml) was added dropwise over a 15-min period to a stirred solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**3**) (1.00 g, 4.90 mmol) in methylene chloride (15 ml). After the reaction mixture was refluxed for 24 hr, the solvent was removed and the remaining white solid, mp 128–135°, was recrystallized from 95% ethanol to give 0.85 g (72%) of 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**18**): mp 139–142°; ir (KBr) 1695 (>C=O), 1300, 1110 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.07 (m, 1, C_9 H), 7.66 (m, 3, C_6, C_7, C_8 H's), 4.90 (dd, J = 2.5 and 7 Hz, 1, >CHCl), 3.9–2.5 (m, 4, $-SO_2CH_2CH_2-$). An analytical sample melted at 143–144°.

Anal. Calcd for $C_{10}H_9ClO_3S$: C, 49.08; H, 3.77; Cl, 14.49. Found: C, 48.91; H, 3.49; Cl, 14.67.

Method B.—A solution of 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**17**) (137 mg, 0.64 mmol) in $CHCl_3$ (4 ml) was added dropwise to a solution of *m*-chloroperbenzoic acid (330 mg, 1.9 mmol) in $CHCl_3$ (6 ml) maintained at −20° and the reaction mixture was allowed to come to room temperature and stirred overnight. The reaction solution was washed with 10% $NaHCO_3$ and H_2O and dried, and the solvent was removed. The residue (157 mg, mp 110–120°) was recrystallized from ethanol and gave 105 mg (66%) of 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**18**), mp 143–144°. A mixture melting point with a sample from method A was not depressed and the nmr spectra of both samples were identical.

***cis*- and *trans*-4-Bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (11 and 12). Method A.**—After a mixture of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**) (5.00 g, 19.50 mmol), *N*-chlorosuccinimide (2.67 g, 20.00 mmol), and CCl_4 (60 ml), placed in a flask protected with a $CaCl_2$ drying tube, was stirred at room temperature for 24 hr, the succinimide was filtered and removal of the solvent under vacuum left 1.58 g of solid. The crude solid was placed in $CHCl_3$ (5 ml) and the insoluble cis isomer was filtered. The filtrate was cooled and gave an additional amount of cis isomer. Recrystallization of the combined solids from hexane–$CHCl_3$ gave 0.40 g (7%) of *cis*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**11**): mp 134–135°; ir (KBr) 1685 cm^{-1} (>C=O); nmr ($CDCl_3$) δ 7.71–7.40 (m, 4, aromatic H's), 5.37 (dd, 1, $J_{C_4-C_{3x}}$ = 6, $J_{C_4-C_{3y}}$ = 8 Hz, –COCHBr–), 4.72 (dd, 1, $J_{C_2-C_{3x}}$ = 4, $J_{C_2-C_{3y}}$ = 12 Hz, –SCHCl–), 3.18 (two dd, 1, $J_{C_{3x}-C_{3y}}$ = 14, $J_{C_{3x}-C_4}$ = 6, $J_{C_{3x}-C_2}$ = 4 Hz, $-SCHClCH_xH_yCHBr$), 2.57 (two dd, 1, $J_{C_{3y}-C_{3x}}$ = 14, $J_{C_{3y}-C_2}$ = 12, $J_{C_{3y}-C_4}$ = 8 Hz, $-SCHClCH_xH_yCHBr$).

The above chloroform solution was evaporated to dryness and the residue was recrystallized from hexane–$CHCl_3$ to give 1.00 g (18%) of *trans*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**12**): mp 98–99°; ir (KBr) 1695 cm^{-1} (>C=O); nmr ($CDCl_3$) δ 7.75–7.28 (m, 4, aromatic H's), 5.25 (dd, 1, $J_{C_4-C_{3x}}$ = 6.5, $J_{C_4-C_{3y}}$ = 8.5 Hz, –COCHBr–), 5.02 (dd, 1, $J_{C_2-C_{3x}}$ = 6.5, $J_{C_2-C_{3y}}$ = 5.5 Hz, –SCHCl), 2.96 (dd, C_{3x} and C_{3y} overlap, $J_{C_{3x}-C_4}$ = 6.5, $J_{C_{3x}-C_2}$ = 6.5 Hz, $-SCHClCH_x-H_yCHBr$–), 2.92 (dd, C_{3y} and C_{3x} overlap, $J_{C_{3y}-C_4}$ = 8.5, $J_{C_{3y}-C_2}$ = 5.5 Hz, $-SCHClCH_xCH_yCHBr$–).

Anal. Calcd for $C_{10}H_8BrClOS$: C, 41.19; H, 2.76; Br, 27.41. Found for cis isomer C: 41.43; H, 2.83; Br, 27.35. Found for trans isomer C: 41.00; H, 2.66; Br, 27.74.

Method B.—Sulfuryl chloride (1.08 g, 8.00 mmol) was added dropwise over a period of 10 min to a stirred solution of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**) (2.00 g, 7.80 mmol) in CH_2Cl_2 (25 ml) at room temperature. The reaction mixture was refluxed (opening fitted with a $CaCl_2$ drying tube) for 1 hr, and the solvent was removed under vacuum to give 1.42 g (63%) of a mixture of the cis and trans isomers. A trace amount of the cis isomer was removed by treating the crude material with cold $CHCl_3$ (3 ml) and filtering off the insoluble cis isomer **11**. The solvent was removed from the filtrate and recrystallization of the residue from hexane–$CHCl_3$ gave 1.35 g (61%) of *trans*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**12**), mp 98–99°. The ir and nmr spectra and mixture melting point were identical with those of the trans isomer isolated by method A.

***cis*-4-Bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-Dioxide (13).**—A solution of *cis*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**11**) (0.37 g, 1.27 mmol) in $CHCl_3$ (6 ml) was added to a stirred solution of *m*-chloroperbenzoic acid (0.50 g, 2.29 mmol) in $CHCl_3$ (8 ml) maintained at −10 to −15°. The reaction mixture was allowed to warm to room temperature and stirred for 9 hr. Work-up by the procedure described for the cis dichloro ketone sulfone **9** and recrystallization of the crude product from 95% ethanol gave 0.36 g (87%) of *cis*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**13**): mp 167–169°; ir (KBr) 1700 (>C=O), 1330 and 1170, 1120 cm^{-1} (three strong bands) (>SO_2); nmr (CD_3COCD_3) δ 8.13–7.65 (m, 4, aromatic H's), 5.65 (dd, 1, $J_{C_4-C_3}$ = 10, $J_{C_4-C_3}$ = 6 Hz, –COCHBr–), 5.23 (dd, 1, $J_{C_2-C_3}$ = 12, $J_{C_2-C_3}$ = 3 Hz, $-SO_2CHCl$–), 3.74–3.20 (m, 2, $-SO_2CHClCH_2CHBr$–).

Anal. Calcd for $C_{10}H_8BrClO_3S$: C, 37.11; H, 2.49; O, 14.83. Found: C, 37.09; H, 2.42; O, 14.51.

***trans*-4-Bromo-1-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-Dioxide (14). Method A.**—Using the preceding procedure (*cis*-4-bromo-2-chloro sulfone **13**,) *m*-chloroperbenzoic acid (1.35 g, 7.86 mmol) in $CHCl_3$ (20 ml) and *trans*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**12**) (1.00 g, 3.43 mmol) in $CHCl_3$ (10 ml) gave after recrystallization from 95% ethanol 0.92 g (83%) of *trans*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**14**): mp 161–163° dec; ir (KBr) 1705 (>C=O), 1330, 1145, and 1120 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.13 (m, 1, C_9 H), 7.91–7.50 (m, 3, C_6,C_7,C_8 H's), 5.22 (dd, 1, $J_{C_4-C_3}$ = 5, $J_{C_4-C_3}$ = 6 Hz, –COCHBr–), 5.00 (dd, 1, $J_{C_2-C_3}$ = 6, $J_{C_2-C_3}$ = 5 Hz, $-SO_2CHCl$–), 3.06 (dd, 2, J = 5, 6 Hz, $-SO_2-CHClCH_2CHBr$–).

Anal. Calcd for $C_{10}H_8BrClO_3S$: C, 37.11; H, 2.49; O, 14.83. Found: C, 37.43; H, 2.56; O, 15.02.

Method B.—Using the procedure described under *trans*-2,4-dichloro keto sulfone **10** (method A), *cis*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**13**) (200 mg, 0.62 mmol) and triethylamine (0.72 g, 7.2 mmol) in $CHCl_3$ (5 ml) gave 190 mg of crude solid, mp 160–163°. Recrystallization of the crude solid from 95% ethanol gave 183 mg (92%) of *trans*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**14**), mp 161–163°. The ir and nmr spectra and mixture melting point were identical with those of the trans isomer isolated by method A.

4-Iodo-3,4-dihydro-1-benzothiepin-5(2*H*)-one.—A solution of 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**2**) (9.5 g, 0.036 mol), KI (15 g, 0.10 mol), and acetone (60 ml) was refluxed for 90 min, poured into water, and extracted with ether and the extract was dried (anhydrous K_2CO_3). After the solvent was

(18) The nmr peaks used to calculate this ratio involved a comparison of the low-field triplet (δ 5.5) for the cis isomer **6** with the entire absorption (δ 5.7–4.7) of the C_2 H and C_4 H of both **6** and **7**. The trans isomer **7** was clearly the more abundant component from comparison of its low-field doublets of doublets (δ 5.29) with that of the cis **6** low field triplet (δ 5.5). Overlapping C_2 H and C_4 H protons of the trans isomer **7** precluded a more accurate analysis of the isomer composition.

removed, the red solid was recrystallized twice from methanol and gave 7.5 g (65%) of faintly yellow 4-iodo-3,4-dihydro-1-benzothiepin-5(2*H*)-one, mp 98–99°.

Anal. Calcd for $C_{10}H_9IOS$: C, 39.49; H, 2.98. Found: C, 39.93; 39.75; H, 3.10, 3.09.

Registry No.—**1**, 21609-70-1; **2**, 21609-66-5; **3**, 22710-97-0; **3**, 22710-97-0; **4**, 21609-67-6; **5**, 40322-27-8; **6**, 40322-28-9; **7**, 40322-29-0; **7**, 40322-29-0; **8**, 40322-30-3; **9**, 40322-31-4; **10**, 40322-32-5; **11**, 40322-33-6; **12**, 40322-34-7; **13**, 40322-35-8; **14**, 40322-36-9; **15**, 40322-37-0; **16**, 40322-38-1; **17**, 40322-39-2; **18**, 40322-63-2; bromine, 7726-95-6; *N*-chlorosuccinimide, 128-09-6; sulfuryl chloride, 7791-25-5; *m*-chloroperbenzoic acid, 937-14-4; lithium chloride, 7447-41-8; dimethylformamide, 68-12-2; 4-iodo-3,4-dihydro-1-benzothiepin-5(2*H*)-one, 40322-40-5.

Seven-Membered Heterocycles. VI. 4-Alkylidene-1-benzothiepin-5(2*H*)-ones and the Reaction of Halogenated 3,4-Dihydro-1-benzothiepin-5(2*H*)-ones with Base[1-3]

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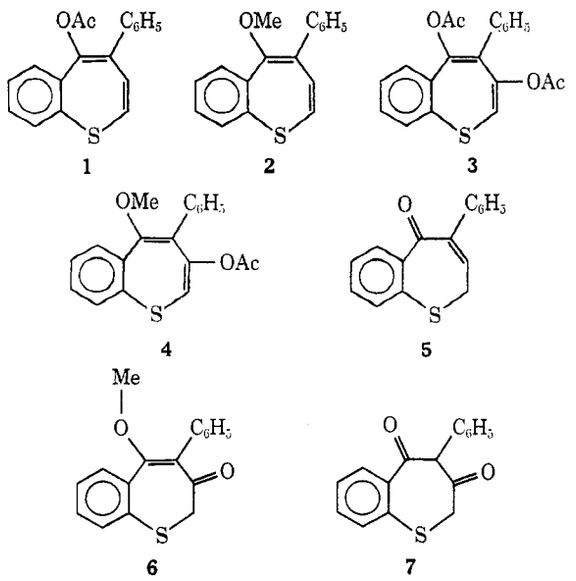
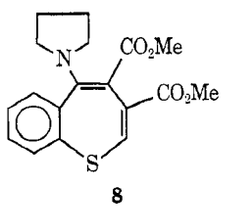
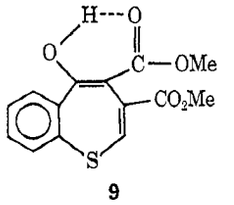
The Mannich reaction with 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**15**) and dimethylamine hydrochloride provided 4-[(dimethylamino)methyl]-3,4-dihydro-1-benzothiepin-5(2*H*)-one hydrochloride (**16**) and a dimer **17** of 4-methylene-1-benzothiepin-5(2*H*,3*H*)-one, while base-catalyzed condensation of benzaldehyde with **15** gave 4-(α-hydroxybenzyl)-3,4-dihydro-1-benzothiepin-5-(2*H*)-one (**19**), 4-benzylidene-1-benzothiepin-5(2*H*,3*H*)-one (**20**), or 4,4′-benzylidenebis[3,4-dihydro-1-benzothiepin-5(2*H*)-one] (**18**) depending on temperature and solvent. Condensation of **15** and ethyl formate produced the hydroxymethylene derivative **21** which formed an enamine **22** with morpholine. Reaction of the enamine **22** with phenylmagnesium bromide and methylmagnesium iodide formed **20** and 4-ethylidene-1-benzothiepin-5(2*H*,3*H*)-one (**23**), respectively. Attempts to isomerize the exocyclic double bond in **20** and **23** using Pd/C were unsuccessful. Reaction of 4-bromo- (**12**, X = Br) or 4-iodo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**12**, X = I) with a variety of bases failed to produce 1-benzothiepin-5(2*H*)-one (**13**), while reaction of *cis*- or *trans*-2,4-dichloro-1-benzothiepin-5(2*H*)-one (**27a** and **27b**, respectively) with base rapidly formed 7a-chlorocyclopropa[*b*][1]benzothiopyran-7-one (**28**). Base-catalyzed elimination of hydrogen chloride from *cis*- and *trans*-2-chloro-4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**29a**, and **29b**, respective) gave the corresponding bromocyclopropyl ketone (**30**). The effect of base and solvent on the 1,3 elimination is reviewed and the enolate ion was trapped as the enol acetate **34**. The acid-catalyzed ring opening of the chlorocyclopropyl ketone **28** with acetic anhydride provided 2,5-diacetoxy-4-chloro-2,3-dihydro-1-benzothiepin (**39**) and similar ring-opening reactions with 7a-chloro-7-hydroxycyclopropa[*b*][1]benzothiopyran (**41**) and hydrogen chloride or acetic anhydride and *p*-toluenesulfonic acid gave 2,4-dichloro- (**45**) or 2-acetoxy-4-chloro-2,3-dihydro-1-benzothiepin (**43**). The formation of these compounds is explained *via* homoallylic cations **40** and **47**. Compound **45** and its derivatives are useful intermediates in the synthesis of 1-benzothiepin.

The stable 1-benzothiepin derivatives, reported in the literature,[5,6] have been highly substituted on the thiepin ring and contained one or more methoxy and/or acetoxy groups (compounds **1–4**). These derivatives were prepared by the methylation or acetylation of the corresponding enols of compounds **5–7**. A recent addition to the class of isolable 1-benzothiepins was dimethyl 5-pyrrolidino-1-benzothiepin-3,4-dicarboxylate (**8**) and the corresponding 5-hydroxy derivative **9**.[7]







It is interesting to note that compounds **5–7** existed in the keto form while **9** was exclusively enolic. A sta-

(1) For part V in this series see V. J. Traynelis, J. C. Sih, Y. Yoshikawa, R. F. Love, and D. M. Borgnaes, *J. Org. Chem.*, **38**, 2623 (1973).

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(4) (a) Abstracted from a portion of the Ph.D. Dissertation submitted by J. C. S. in Dec 1971 at West Virginia University. (b) Abstracted from a portion of the Ph.D. Dissertation submitted by D. M. B. in Aug 1968 at the University of Notre Dame.

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