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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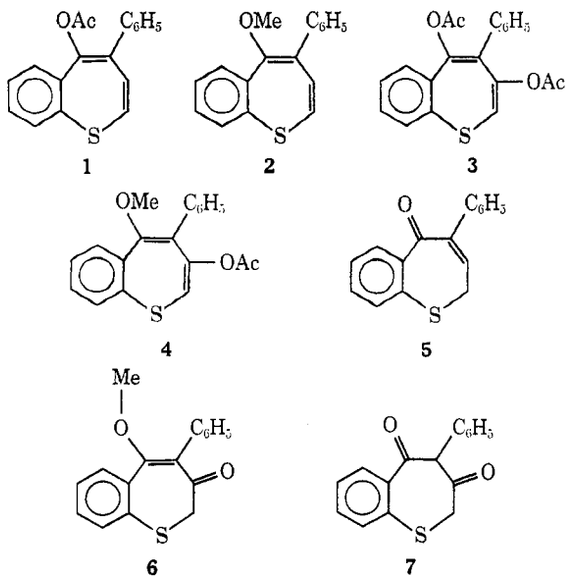
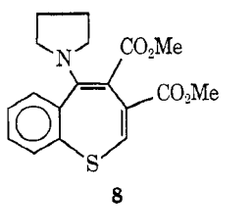
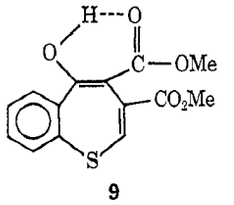
The Mannich reaction with 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**15**) and dimethylamine hydrochloride provided 4-[(dimethylamino)methyl]-3,4-dihydro-1-benzothiepin-5(2*H*)-one hydrochloride (**16**) and a dimer **17** of 4-methylene-1-benzothiepin-5(2*H*,3*H*)-one, while base-catalyzed condensation 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).

(2) Presented in part before the Organic Division at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

(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) (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.

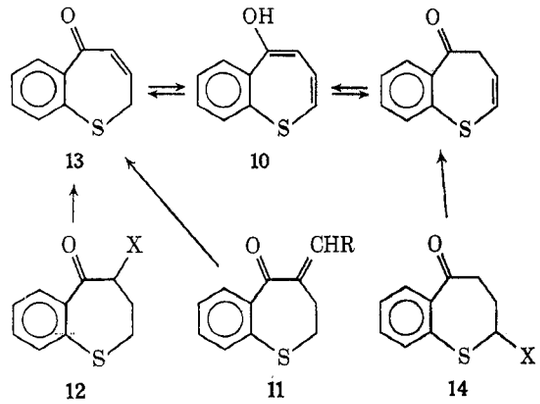
(5) H. Hofmann and H. Westernacher, *Chem. Ber.*, **102**, 205 (1969).

(6) H. Hofmann, B. Meyer, and P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, **11**, 423 (1972).

(7) D. N. Reinhoudt and C. G. Kouwenhoven, *Chem. Commun.*, 1233 (1972).

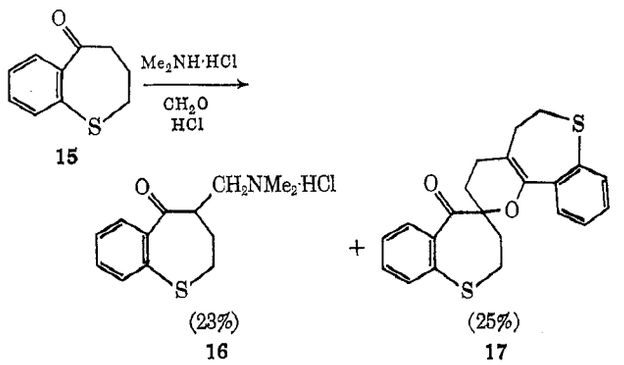
bilizing feature in **9** has been ascribed to intramolecular H bonding.[7]

In this report we wish to describe our studies directed toward unsaturated ketones in the 1-benzothiepin system. The three types of precursors (**11**, **12**, **14**) which can ultimately lead to derivatives of 5-hydroxy-1-benzothiepin (**10**) are outlined below. Although we

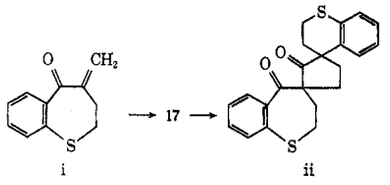


were not successful in producing and trapping **10** *via* a derivative, some unexpected reactions of the halogenated ketones led to intermediates which were subsequently converted to 1-benzothiepins.

The Mannich reaction of 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**15**) and dimethylamine hydrochloride provided the expected product **16** in low yield along with a white, crystalline substance assigned structure **17**.[8-10] When the reaction was performed in acetic acid, only **17** was formed (86% yield). The use of **16** as a source of 4-methylene-1-benzothiepin-5(2*H*,3*H*)-one was precluded owing to the ease of dimerization of the unsaturated ketone to **17**.



(8) 2′,3,3′,4,5′,6′-Hexahydrospiro[1-benzothiepin-4,2′-(1-benzothiepino-[5,4-*b*]-4H-pyran)]-5(2*H*)-one. Compound **17** is also available by heating the free base 4-[(dimethylamino)methyl]-3,4-dihydro-1-benzothiepin-5-(2*H*)-one. The proposed formation of compound **17** entailed a Diels–Alder dimerization of 4-methylene-1-benzothiepin-5(2*H*,3*H*)-one (i),[9,10] which can form by elimination of dimethylamine from the Mannich product. An alternate structure ii has been suggested[10] which arises from an acid-catalyzed rearrangement of i. Thus the structural assignment for **17** remains unsettled.

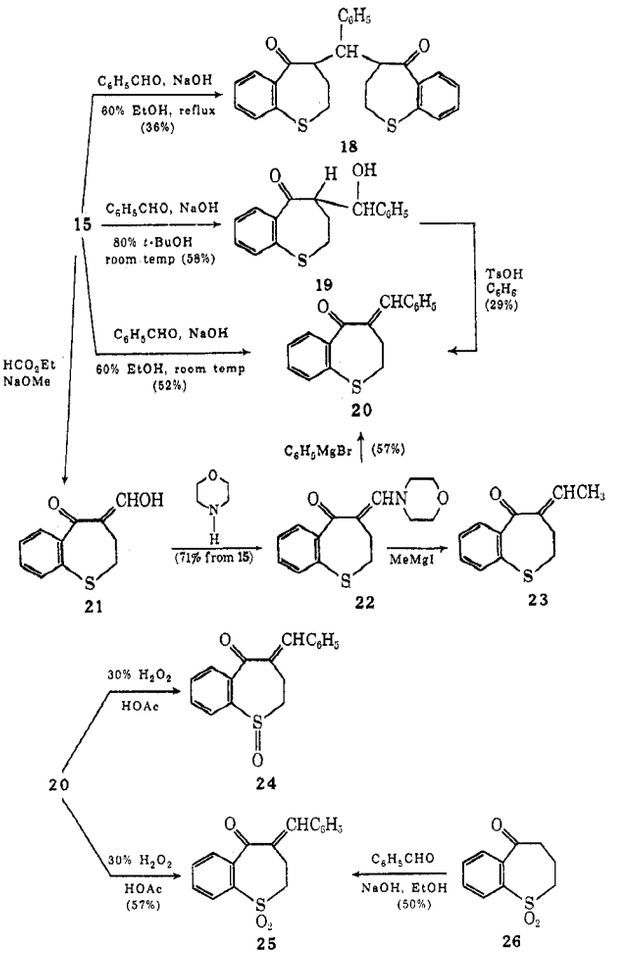


(9) R. J. Mohrbacher, U. S. Patent 3,287,369 (1966); *Chem. Abstr.*, **66**, 28754k (1967).

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

The base-catalyzed reaction of **15** and benzaldehyde 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**) which depended on the reaction temperature and solvent. An acid-catalyzed dehydration of **19** also provided **20**, although in low yield. An alternative sequence used to prepare **20** employed the method of Ireland[11] for generating α-alkylidene ketones. The condensatiou of **15** and ethyl formate produced the hydroxymethylene derivative **21**, which showed a strong, broad ir absorption with peaks at 1629 and 1585 cm^{-1}, characteristic for α,β-unsaturated β-hydroxy ketones,[11,12] Reaction of **21** with morpholine gave enamine **22** which, when treated with phenylmagnesium bromide, was converted to **20**. This enamine synthesis was also utilized in the preparation of 4-ethylidene-1-benzothiepin-5(2*H*,3*H*)-one (**23**).

Oxidation of **20** with hydrogen peroxide at room temperature gave the corresponding sulfoxide **24**, while more vigorous oxidizing conditions led to sulfone **25**, which was also prepared by the base-catalyzed condensation of benzaldehyde and 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**26**).



Structural assignments for the above condensation products and their oxidized derivatives were based on uv (see Table I), ir, and nmr spectral data. The uv

(11) R. Ireland and P. Schiess, *J. Org. Chem.*, **28**, 6 (1963).

(12) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, pp 142–143.

TABLE I
UV SPECTRAL DATA[a]

Compd	λ_{max}, nm	Log ε
4-Benzylidene-1-benzothiepin-5(2*H*,3*H*)-one (**20**)	235	4.07
	304	4.20
4-Benzylidene-1-benzothiepin-5(2*H*,3*H*)-one 1-oxide (**24**)	233	4.22
	316	4.16
4-Benzylidene-1-benzothiepin-5(2*H*,3*H*)-one 1,1-dioxide (**25**)	232	4.04
	305	4.16
4-Ethylidene-1-benzothiepin-5(2*H*,3*H*)-one (**23**)	251	4.16
4-(Morpholinomethylene)-1-benzothiepin-5-(2*H*,3*H*)-one (**22**)	247	4.06
4-(α-Hydroxybenzyl)-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**19**)	240	4.28
	263	3.75
trans-Benzalacetophenone	227[b]	
	305	4.40
	226[c]	4.23
	300	4.30
Phenylvinyl ketone	247[d]	4.00

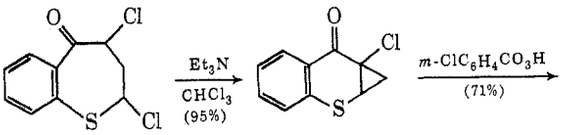
[a] Measurements were made in 95% ethanol unless stated otherwise. [b] Methanol solvent. J. F. Thomas and G. Branch, *J. Amer. Chem. Soc.*, **75**, 4793 (1953). [c] Cyclohexane solvent. C. L. Stevens, R. C. Church, and V. J. Traynelis, *J. Org. Chem.*, **19**, 522 (1954). [d] K. Bowden, E. A. Braude, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 45 (1946).

data supported the α,β-unsaturated ketone structure, while ir absorptions were consistent with functional group changes. In addition the exocyclic nature of the double bond was confirmed by ozonolysis of **25**, which gave benzaldehyde. The other expected ozonolysis product, the α diketone, was not isolated or characterized.

Isomerization of the exocyclic double bonds in **20** and **23** into the ring was studied using the method reported by Leonard[13,14] for isomerization of 3,5-dibenzylidenetetrahydropyrone[13] and α,α′-dibenzylidenecycloheptanone[14] into 3,5-dibenzylpyrone and 2,7-dibenzyltropone, respectively. When **20** or **23** was heated with 10% Pd/C in ethylene glycol at various temperatures and times, no isomerization was observed and the starting material was recovered in 80–88% yields. Even at temperatures of 300° and in the absence of solvent, no isomerization in **20** or **23** occurred; however, some decomposition was noted. Thus, one is led to conclude that no strong driving force exists for relocating the double bond into the ring and generating the enolic structure **10** even when the exocyclic double bond lacks further conjugation as in **23**.

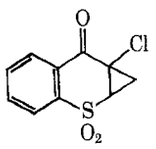
A second approach directed toward the formation of **13** or its derivatives involved the study of the reaction of halogenated ketones with base. The reaction of 4-bromo-[1,15] (**12**, X = Br) or 4-iodo-3,4-dihydro-1-benzothiepin-5-(2*H*)-one[1,4b] (**12**, X = I) with a variety of bases [triethylamine, tetramethylquanidine, potassium *tert*-butoxide, LiBr and dimethylformamide (DMF) or LiCl, Li_2CO_3 in DMF] gave either unreacted starting material or, under more vigorous conditions, resinification. Although hydrogen halide was eliminated in some reactions, no identifiable products could be isolated. The difficulty encountered in the elimination of hydrogen halide in **12** to generate **13** is not surprising in view of the conformational preference in **12**[1] and the high energy state required for a trans coplanar elimination in **12**. The use of **14**, X = Cl, in reactions with base was precluded since it was not possible to obtain **14**, X = Cl, free from the dichloro ketone **27**[1] and thus we directed our studies to **27**.

The reaction of either *cis*- or *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**27a** and **27b**, respectively) with triethylamine in chloroform at room temperature resulted in a rapid 1,3 elimination of hydrogen chloride to give 7a-chlorocyclopropa[*b*][1]benzothiopyran-7-one (**28**) in near-quantitative yields. The



cis, **27a**
trans, **27b**

28



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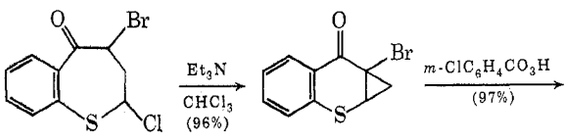
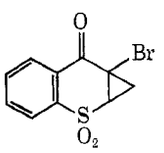


cis, **29a**
trans, **29b**

30



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direction of ring closure, namely abstraction of the C_4 proton and elimination of the C_2 chlorine, was established by reaction of *cis*- or *trans*-2-chloro-4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**29a** and **29b**, respectively) with triethylamine to give 7a-bromocyclopropa[*b*][1]benzothiopyran-7-one (**30**). The cyclopropyl ketones **28** and **30** were oxidized to the corresponding sulfones **31** and **32**, respectively, and the structures were assigned on the basis of elemental analysis, ir, and their unique nmr spectra.

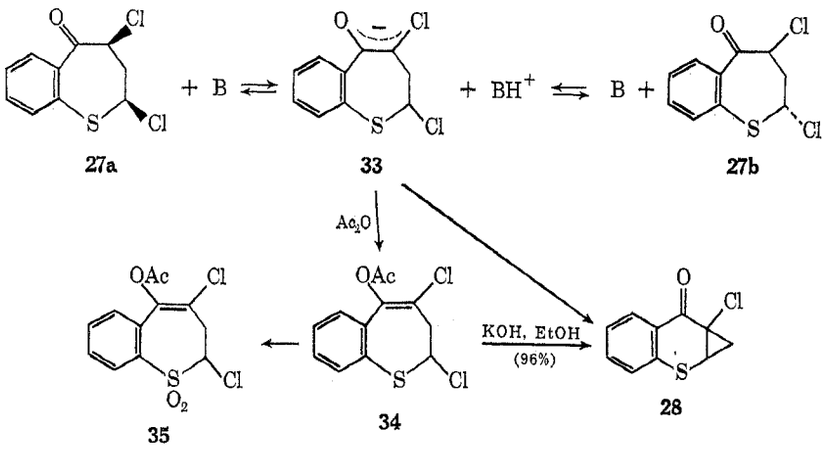
The influence of solvent and base strength on the conversion of the dichloro ketones **27** to the cyclopropyl ketone **28** are summarized in Table II. One finds that an increase in basicity or solvent polarity enhances ring closure to the cyclopropyl ketone **28**. The initial step entails abstraction of the C_4 proton and the formation of enolate ion **33**. With triethylamine in chloroform the elimination of the C_2 chloride from **33** becomes so rapid that the 1,3 elimination resembles an E2 process. Even when limited quantities of triethylamine were used, no isomerization of **27a** to **27b** or vice versa or deuterium exchange in **27** was observed.

(13) N. J. Leonard and D. Choudhury, *J. Amer. Chem. Soc.*, **79**, 156 (1957).
(14) N. J. Leonard, L. A. Miller, and J. W. Berry, *ibid.*, **79**, 1482 (1957).
(15) R. F. Love, Ph.D. Dissertation, University of Notre Dame, May 1960.

TABLE II
REACTIONS OF *cis*- AND *trans*-2,4-DICHLORO-3,4-DIHYDRO-1-BENZOTHIEPIN-5(2*H*)-ONE WITH BASE AT ROOM TEMPERATURE

Isomer (mmol)	Base (mmol)	Solvent (ml)	Reaction time	Yield,[a] % (compd)
cis **27a** or *trans*-**27b** (4.05)	Et_3N (25)	$CHCl_3$ (20)	17 min[b]	100 (**28**)[c]
cis-**27a** (2.22)	Et_3N (1.00)	$CHCl_3$ (10)	5 min	32 (**28**) 68 (**27a**)[d]
trans-**27b** (2.22)	Et_3N (1.00)	$CHCl_3$ (10)	5 min	34 (**28**) 66 (**27b**)
cis-**27a** (5.00)	Pyridine (5.00)	Benzene (17)	21 hr	0 (**28**) Equilibrium mixture of **27a** and **27b**[e]
trans-**27b** (5.00)	Pyridine (5.00)	Benzene (17)	21 hr	0 (**28**) Equilibrium mixture of **27a** and **27b**[e]
cis-**27a** (5.00)	Pyridine (5.00)	$CHCl_3$ (17)	21 hr	72 (**28**) 27 (**27a** and **27b**)
cis-**27a** or *trans*-**27b** (5.00)	Et_3N (5.00)	$CHCl_3$ (17)	21 hr	100 (**28**)
cis-**27a** (4.05)	Et_3N (25)	Benzene (20)	30 min	40 (**28**) 60 (**27a** and **27b**)
cis-**27a** (4.05)	Et_3N (25)	Benzene (20) Ethanol (2)	30 min	100 (**28**)

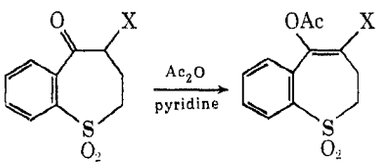
[a] Yields were determined by nmr analysis. [b] When the reaction was followed by nmr, complete conversion to **28** resulted immediately after addition of triethylamine. [c] 7a-Chlorocyclopropa[*b*][1]benzothiopyran-7-one. [d] No isomerization of **27a** to **27b** occurred during the reaction as determined by nmr; no deuterium exchange was observed when the reaction was performed in the presence of deuterio ethanol. [e] When aliquots of the reaction mixture were quenched at the end of 17, 21, or 48 hr, the relative peak heights (nmr) used for analysis of the mixture of **27a** and **27b** remained constant and represented a 50:50 mixture.



On the other hand the reaction of **27a** or **27b** with pyridine in benzene led only to isomerization and formation of an equilibrium mixture of **27a** and **27b**, while the use of pyridine in chloroform or triethylamine in benzene provided some cyclopropyl ketone **28** and the isomerized equilibrium mixture of **27a** and **27b**, thus approaching an E1cB type process.

The initial appearance of enolate ion **33** was established by acetylation and isolation of enol acetate **34**, characterized as its sulfone **35**. When **34** was treated with triethylamine, no reaction took place; however, reaction with potassium hydroxide in 95% ethanol rapidly generated the cyclopropyl ketone **28**, most likely *via* **33**.

Sulfone **35** was also obtained from reaction of *cis*- or *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide[1] with acetic anhydride and pyridine. Other α-halo keto sulfones **36** were readily converted to enol acetates, 5-acetoxy-4-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**37**), and 5-acetoxy-4-bromo-2,3-dihydro-1-benzothiepin 1,1-dioxide (**38**), by action of acetic anhydride and pyridine, while the corresponding α-halo keto sulfides **12** and **15** did not react even under more vigorous conditions.

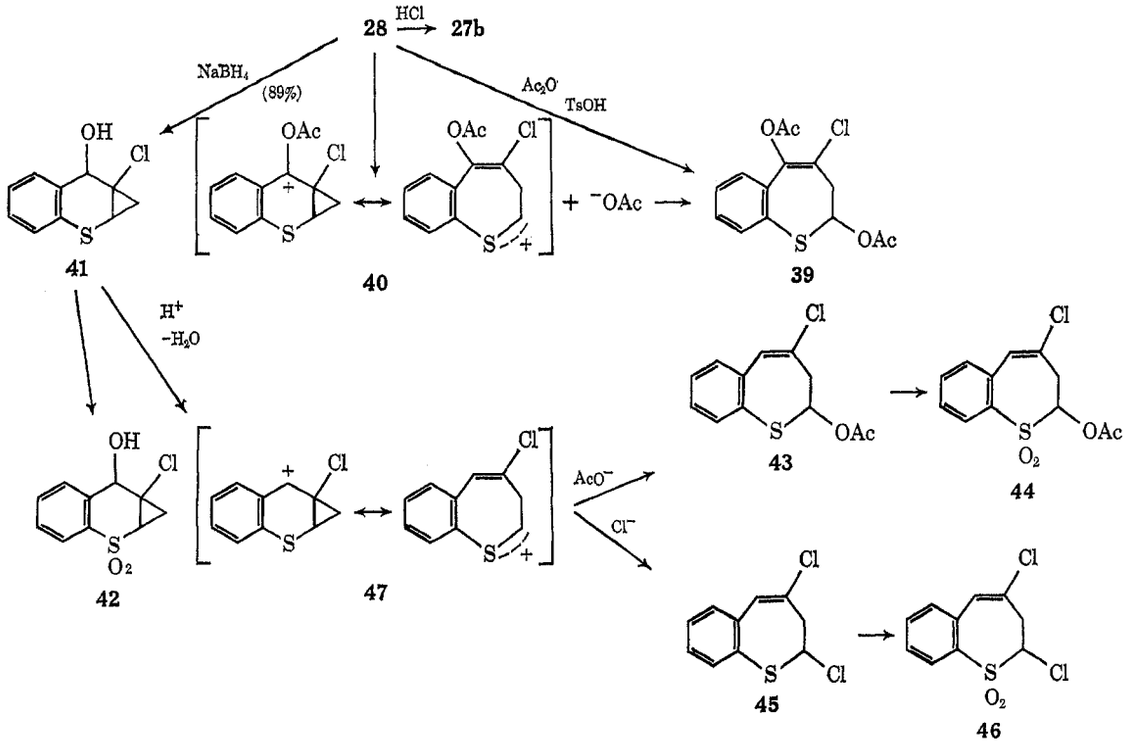


36

37, X = Cl

38, X = Br

Ring opening of the cyclopropane ring in **28** occurred quite readily under acid catalysis to regenerate the 1-benzothiepin system. The reaction of **28** with HCl in chloroform proceeded steroselectively to produce *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one (**27b**).[1] The absence of the cis isomer (**27a**) (which is stable under the experimental conditions for adding HCl to **28**) excludes the enol intermediate and thus requires a cis addition of HCl across the cyclopropane ring. In contrast the addition of acetic anhydride to **28** in the presence of *p*-toluenesulfonic acid gave 2,5-diacetoxy-4-chloro-2,3-dihydro-1-benzothiepin (**39**), which can be rationalized by a similar pathway to the addition of HCl followed by enol acetate formation or by the steps outlined below *via* the homoallylic cation **40**.



Reduction of **28** with sodium borohydride gave 7a-chloro-7-hydroxycyclopropa[*b*][1]benzothiopyran (**41**), which was characterized as it sulfone **42**. The cyclopropyl alcohol **41**, like **28**, underwent facile ring opening under acidic conditions with acetic anhydride and hydrogen chloride to produce **43** and **45**, respectively, which were characterized by their corresponding sulfone **44** and **46**. The formation of the 2,3-dihydro-1-benzothiepins **43** and **45** is readily rationalized *via* cation **47**.

The use of **28** and **41** in the synthesis of substituted 2,3-dihydro-1-benzothiepins can be extended to 5-alkyl or 5-aryl derivatives by application of the Grignard reaction with **28** and HCl ring opening of the resulting cyclopropyl alcohol.[16] These 2-chloro-2,3-dihydro-1-benzothiepins, such as **45**, have been key intermediates in the synthesis of 1-benzothiepin and its chlorinated derivatives. The preparation and properties of 1-benzothiepin will be reported in the subsequent publication.

Thus the general method for preparing 2-chloro-2,3-dihydro-1-benzothiepin derivatives serves as a good synthetic approach in generating a variety of 1-benzothiepin derivatives.

Experimental Section[17]

4-[(Dimethylamino)methyl]-3,4-dihydro-1-benzothiepin-5(2*H*)-one Hydrochloride (16).—A mixture of 3,4-dihydro-1-benzothiepin-5(2*H*)-one[18] (8.9 g, 0.050 mol), dimethylamine hydrochloride (4.2 g, 0.052 mol), paraformaldehyde (2.3 g, 0.075 mol), isoamyl alcohol (40 ml), and concentrated HCl (0.5 ml) was refluxed for 3.5 hr, concentrated, diluted with H_2O, and extracted with ether. The extract was dried and upon removal of the ether gave 2.4 g (25%) of 2′,3,3′,4,5′,6′-hexahydrospiro-[1-benzothiepin-4,2′-(1-benzothiepino[5,4-*b*]-4*H*-pyran)]-5(2*H*)-one (**17**), mp 152–154°.

The aqueous layer was evaporated, leaving 3.1 g (23%) of crude 4-[(dimethylamino)methyl]-3,4-dihydro-1-benzothiepin-5-(2*H*)-one hydrochloride, mp 169–172°. An analytical sample, mp 176–179°, ir ($CHCl_3$) 2320 (>NH)$^+$, 1695 cm^{-1} (>C=O), nmr (DMSO-d_6) δ 7.86–7.28 (m, aromatic H's), 4.0–1.70 [broad multiplet with overlapping solvent peaks and a singlet at δ 2.67 for the $N(CH_3)_2$ includes all aliphatic protons], was obtained by repeated crystallization from ethanol–ethyl acetate.

Anal. Calcd for $C_{13}H_{18}ClNOS$: C, 57.45; H, 6.67. Found: C, 57.55, 57.43; H, 6.51, 6.74.

2′,3,3′,4,5′,6′-Hexahydrospiro[1-benzothiepin-4,2′-(1-benzothiepino[5,4-*b*]-4*H*-pyran)]-5(2*H*)-one (17).—A solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one[18] (17.8 g, 0.10 mol), ethanol (15 ml), acetic acid (14.0 g, 0.233 mol), aqueous dimethylamine solution (6.75 g, 0.15 mol), and formalin (7.50 g, 0.25 mol) was refluxed for 3 hr and cooled. The resulting solid was filtered, washed with H_2O, and dried, giving 16.5 g (86%) of **17**, mp 152–154°, ir (CCl_4) 1720 (>C=O), 1625 cm^{-1} (>C=C<). An analytical sample of **17**, mp 154.5–155°, was prepared by repeated crystallization from mixed octanes.

Anal. Calcd for $C_{22}H_{20}O_2S_2$: C, 69.44; H, 5.30; mol wt, 380.5. Found: C, 69.44, 69.62; H, 5.41, 5.40; mol wt, 398.

4-(α-Hydroxybenzyl)-3,4-dihydro-1-benzothiepin-5(2*H*)-one (19).—A solution of 80% aqueous *tert*-butyl alcohol (100 ml), NaOH (0.2 g, 0.005 mol), 3,4-dihydro-1-benzothiepin-5(2*H*)-one[18] (8.9 g, 0.050 mol), and benzaldehyde (5.3 g, 0.050 mol) was stirred and, on four occasions at 30-min intervals, the precipitated solid was filtered. The solids were combined and crystallization from benzene gave 15.5 g (58%) of 4-(α-hydroxybenzyl)-3,4-dihydro-1-benzothiepin-5(2*H*)-one: mp 164–166°; ir ($CHCl_3$) 3600 (free OH) 3500 (associated OH), 1680 cm^{-1} (>C=O); uv max (95% EtOH) 240 nm (log ϵ 4.28), 263 (3.75); nmr ($CDCl_3$) δ 7.95–7.17 (m, 4, aromatic H's), 5.25–5.0 [m, 1, $-CH(OH)C_6H_5$], 3.93 {two t, 1, J = 7, 11 Hz, $-COCH[CH(OH)C_6H_5]-$}, 3.20–1.57 (m, 5, remainder of the aliphatic protons and OH). An analytical sample, mp 168.5–169°, was obtained by repeated crystallization from benzene.

Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.92; H, 5.55.

4,4′-Benzylidenebis[3,4-dihydro-1-benzothiepin-5(2*H*)-one] (18).—After a solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one[18] (8.9 g, 0.050 mol), benzaldehyde (5.3 g, 0.050 mol), NaOH (0.2 g, 0.005 mol), and 60% aqueous ethanol (100 ml) was refluxed for 12 hr, the reaction mixture was cooled and filtered.

(16) V. J. Traynelis and D. Cassis, unpublished results.

(17) 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 or a Beckman IR-8 spectrometer, uv spectra were measured on a Bausch and Lomb 505 spectrometer, and nmr spectra were obtained on a Varian Associates Model HA-60 or Model T-60 spectrometer.

(18) V. J. Traynelis and R. F. Love, *J. Org. Chem.*, **26**, 2728 (1961).

The resulting solid was recrystallized from dioxane–H_2O and gave 4.0 g (36%) of 4,4'-benzylidenebis[3,4-dihydro-1-benzothiepin-5(2*H*)-one], mp 204–205°.

Anal. Calcd for $C_{27}H_{24}O_2S_2$: C, 72.92; H, 5.44; mol wt, 444.62. Found: C, 72.82; H, 5.81; mol wt, 444.

4-Benzylidene-1-benzothiepin-5(2*H*,3*H*)-one (20). Method A.—A solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one[18] (8.9 g, 0.050 mol), benzaldehyde (5.3 g, 0.050 mol), NaOH (0.2 g, 0.005 mol), and 60% aqueous ethanol (100 ml) was allowed to remain for 30 min at room temperature with occasional swirling. The resulting solid was filtered, washed (H_2O), and dried and recrystallization from methanol gave 7.0 g (52%) of 4-benzylidene-1-benzothiepin-5(2*H*,3*H*)-one as yellow needles: mp 82–84°; uv max (95% EtOH) 235 nm (log ϵ 4.07), 304 (4.20); ir (CCl_4) 1675 (C=O), 1610 cm^{-1} (C=C); nmr (CCl_4) δ 8.06 (s, 1, C=CHC_6H_5), 7.35 (m, 9, aromatic H's), 3.02 (m, 4, $-SCH_2-CH_2-$). Repeated crystallization from methanol gave an analytical sample, mp 88.5–89°.

Anal. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.82; H, 5.26.

Method B.—To a stirred solution of phenylmagnesium bromide, prepared from bromobenzene (28.6 g, 0.167 mol) and magnesium (4.0 g, 0.17 g-atom) in ether (150 ml), was added solid 4-(morpholinomethylene)-1-benzothiepin-5(2*H*,3*H*)-one (see below for preparation) (10.0 g, 0.0364 mol) and the reaction mixture was stirred at reflux for 4 hr. The solution was hydrolyzed cautiously with 9.1 g of NH_4Cl in 30 ml of H_2O. After the ether layer was separated and dried ($MgSO_4$) and the solvent was removed, the residue was crystallized from methanol and give 5.5 g (57%) of 4-benzylidene-1-benzothiepin-5(2*H*,3*H*)-one, mp 86.5–88°. An ir spectrum of this material was identical with that of the preceding sample.

Method C.—A solution of 4-(α-hydroxybenzyl)-3,4-dihydro-1-benzothiepin-5(2*H*)-one (10.0 g, 0.035 mol) and *p*-toluenesulfonic acid (0.20 g) in benzene (50 ml) was refluxed for 48 hr, after which time 0.42 ml of H_2O was collected in a Dean–Stark trap. The benzene solution was extracted with $NaHCO_3$ solution and washed with water, and after the solvent was removed, the residue was crystallized from methanol. The yield of 4-benzylidene-1-benzothiepin-5(2*H*,3*H*)-one, mp 86–88°, was 2.7 g (29%). A mixture melting point with an authentic sample was not depressed.

4-Benzylidene-1-benzothiepin-5(2*H*,3*H*)-one 1-Oxide (24).—A solution of 4-benzylidene-1-benzothiepin-5(2*H*,3*H*)-one (2.7 g, 0.010 mol), 30% hydrogen peroxide (2.0 g, 0.030 mol), and acetic acid (20 ml) was allowed to stand for 12 hr at room temperature and poured onto cracked ice. The oil which separated crystallized after addition of a few drops of Skelly B. The solid precipitate was filtered, dried, and recrystallized from benzene–Skelly B to give 4-benzylidene-1-benzothiepin-5(2*H*,3*H*)-one 1-oxide: mp 137–140°; uv max (95% EtOH) 233 nm (log ϵ 4.22), 316 (4.16); ir (CCl_4) 1673 (>C=O), 1070 cm^{-1} (>S=O); nmr ($CDCl_3$) δ 8.20–7.30 (m, 10, aromatic H's and >C=C-HC_6H_5), 4.20–2.40 (m, 4, $-SOCH_2CH_2-$).

Anal. Calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00. Found: C, 72.07; H, 4.93.

4-Benzylidene-1-benzothiepin-5(2*H*,3*H*)-one 1,1-Dioxide (25). Method A.—After a solution of 30% hydrogen peroxide (2.0 g, 0.030 mol) and 4-benzylidene-1-benzothiepin-5(2*H*,3*H*)-one (2.7 g, 0.010 mol) in glacial acetic acid (20 ml) remained at room temperature for 12 hr, a second portion of 30% hydrogen peroxide (2.0 g, 0.030 mol) was added and the reaction mixture was heated on a steam bath for 3 hr. The reaction mixture was cooled, poured on ice, and extracted with $CHCl_3$ and the extract was dried ($MgSO_4$). After the solvent was removed, crystallization of the residue from methanol gave 1.7 g (57%) of 4-benzylidene-1-benzothiepin-5(2*H*,3*H*)-one 1,1-dioxide: mp 153–155°; uv max (95% EtOH) 232 nm (log ϵ 4.04), 305 (4.16); ir ($CHCl_3$) 1678 (>C=O), 1332 and 1149 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.10 (s, 1, >C=CHC_6H_5), 8.00–7.40 (m, 9, aromatic H's), 3.57 (t, 2, J = 6 Hz, $-SO_2CH_2CH_2-$), 2.88 (t, 2, J = 6 Hz, $-SO_2-CH_2CH_2-$). Several recrystallizations from methanol gave the analytical sample, mp 156–157°.

Anal. Calcd for $C_{17}H_{14}O_2S$: C, 68.44; H, 4.73. Found: C, 68.48; H, 4.92.

Method B.—A solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide[18] (12.4 g, 0.059 mol), benzaldehyde (6.25 g, 0.059 mol), and NaOH (0.80 g, 0.020 mol) in ethanol (50 ml) was kept at room temperature for 1 hr and then neutralized with hydrochloric acid. The solvent was removed from the reaction mixture and the residue was recrystallized three times from ethanol to give 7.0 g (50%) of 4-benzylidene-1-benzothiepin-5-(2*H*,3*H*)-one 1,1-dioxide, mp 148–150°. Two additional recrystallizations raised the melting point to 154–155°. A mixture melting point with the above sample was not depressed.

Ozonolysis of 4-Benzylidene-1-benzothiepin-5(2*H*,3*H*)-one 1,1-Dioxide.—Ozone (1%) in a stream of oxygen was bubbled into a Dry Ice–acetone-cooled solution of 4-benzylidene-1-benzothiepin-5(2*H*,3*H*)-one 1,1-dioxide (1.0 g, 0.0034 mol) in methylene chloride (100 ml) and pyridine (2 ml) for 3 hr. After the reaction mixture was warmed to room temperature and washed with 10% HCl, $NaHCO_3$ solution, and then H_2O, the organic layer was allowed to react for 2 hr with a solution of sodium metabisulfite (5.0 g) in H_2O (20 ml). The water layer was separated and neutralized with NaOH and the solution was extracted with ether. After the ether solution was dried ($MgSO_4$) and the solvent removed, the residue was treated with 2,4-dinitrophenylhydrazine. The yield of the 2,4-dinitrophenylhydrazone of benzaldehyde, mp 236–238°, was 0.57 g (60%). A mixture melting point with an authentic sample was 236–238°.

A red oil which was isolated from the organic phase of the bisulfite reaction was not identified.

4-Morpholinomethylene-1-benzothiepin-5(2*H*,3*H*)-one (22).—A solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one[18] (7.65 g, 0.0430 mol) and ethyl formate (18.5 g, 0.280 mol) in dry benzene (50 ml) was added slowly to an ice-cooled suspension of sodium methoxide (8.90 g, 0.165 mol) in dry benzene (150 ml). The reaction mixture was stirred overnight at room temperature, H_2O (75 ml) was added, and the aqueous layer was separated. The benzene solution was extracted with 5% NaOH (2 × 25 ml) and the combined alkaline aqueous solutions were washed with ether, cooled, acidified with cold 10% HCl, and extracted with ether. The combined ether extracts were washed with H_2O and saturated NaCl solution and dried (Na_2SO_4). After the ether was removed, the residue was 4-hydroxymethylene-1-benzothiepin-5-(2*H*,3*H*)-one (**21**), an oil, ir (neat) 3400 (–OH), 1730 (medium) (>C=O), 1629 and 1585 cm^{-1} (>C=CHOH).

Without further purification **21** was combined with morpholine (4.35 g, 0.0512 mol) in benzene (120 ml) and the solution was refluxed for 2 hr, during which time H_2O (0.8 ml) was collected in the Dean–Stark trap. The reaction mixture was concentrated to half the original volume and *n*-hexane (50 ml) was added. The resulting solid was filtered and dried and gave 8.4 g (71% based on starting 3,4-dihydro-1-benzothiepin-5(2*H*)-one) of 4-morpholinomethylene-1-benzothiepin-5(2*H*,3*H*)-one, mp 165–167°, ir ($CHCl_3$) 1650 cm^{-1} (>C=O). An analytical sample was prepared by repeated crystallizations from benzene–*n*-hexane, mp 166–167°.

Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.43; H, 6.22. Found: C, 65.66; H, 6.25.

4-Ethylidene-1-benzothiepin-5(2*H*,3*H*)-one (23).—To a solution of methylmagnesium iodide, prepared from magnesium (4.0 g, 0.17 g-atom) and methyl iodide (25.8 g, 0.182 mol) in ether (100 ml), was added in small increments solid 4-morpholinomethylene-1-benzothiepin-5(2*H*,3*H*)-one (10.0 g, 0.0364 mol). After the reaction mixture was stirred for 4.5 hr, NH_4Cl (9.1 g) in H_2O (30 ml) was added followed by more H_2O (100 ml). The organic layer was separated and dried (Na_2SO_4) and the solvent was removed. The residue was crystallized from Skelly B and gave 5.3 g (72%) of 4-ethylidene-1-benzothiepin-5(2*H*,3*H*)-one, mp 75–79°. An analytical sample was obtained by recrystallization from Skelly B and had the following constants: mp 79–79.5°; uv max (95% EtOH) 251 nm (log ϵ 4.16); ir (neat) 1675 cm^{-1} (>C=O); nmr (CCl_4) δ 7.39 (m, 4, aromatic H's), 6.94 (q, 1, J = 7.5 Hz, C=CHCH_3), 2.75 (m, 4, $-SCH_2CH_2-$), 1.89 (d, 3, J = 7.5 Hz, C=CHCH_3).

Anal. Calcd for $C_{12}H_{12}OS$: C, 70.55; H, 5.92. Found: C, 70.42, 70.29; H, 5.91, 5.85.

Attempted Isomerization of 4-Benzylidene-1-benzothiepin-5-(2*H*,3*H*)-one and 4-Ethylidene-1-benzothiepin-5(2*H*,3*H*)-one. Method A.—A mixture of 4-benzylidene-1-benzothiepin-5(2*H*,-3*H*)-one (2.66 g, 0.0100 mol), 10% Pd/C (1.3 g), and ethylene glycol (75 ml) was refluxed for 15 min and filtered hot. After the filtrate was diluted with water and extracted with ether, the ether extract was washed with H_2O and saturated NaCl solution and dried ($MgSO_4$). The ether was removed and the residue upon recrystallization from methanol gave 2.10 g (80%) of recovered starting material, mp 85–87°.

The same procedure was used with 4-ethylidene-1-benzothiepin-5(2*H*,3*H*)-one (1.70 g, 0.00833 mol) and 10% Pd/C (1.00 g) in

ethylene glycol (50 ml) and a 90-min reflux. Starting material was recovered in 88% yield.

Method B.—A mixture of 4-benzylidene-1-benzothiepin-5-(2*H*,3*H*)-one (1.00 g, 0.00376 mol) and 10% Pd/C (0.200 g) was heated in a Wood's metal bath at 250° for 15 min. The reaction mixture was cooled, dissolved in methanol, and filtered and, after the methanol was removed, 0.82 g (82%) of the starting material, mp 85–88°, was recovered. When the reaction was repeated at 300°, 83% of the starting material was recovered.

Similar experiments performed with 4-ethylidene-1-benzothiepin-5(2*H*,3*H*)-one at 250 and 300° gave recovered starting material in 75 and 76% yields, respectively.

7a-Chlorocyclopropa[*b*][1]benzothiopyran-7-one (28).[19] **Method A.**—After a solution of triethylamine (13.1 g, 0.128 mol) and *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one[1] (5.00 g, 0.020 mol) in $CHCl_3$ (70 ml) was allowed to stand at room temperature for 1 hr, the reaction mixture was washed with 10% HCl and H_2O, and the organic layer was dried ($MgSO_4$). The solvent was removed under vacuum and the residual oil solidified upon the addition of ice water. The solid was filtered, dried, and recrystallized from 60% ethanol to give 4.03 g (95%) of 7a-chlorocyclopropa[*b*][1]benzothiopyran-7-one: mp 61–62°; ir (KBr) 3040 (w), 1680 (s, >C=O), 1585 (s), 1310 (s), 1145 (s), 940 (s), 740 (s), 675 cm^{-1} (s); nmr ($CDCl_3$) δ 8.06–7.88 (m, 1, C_3 H), 7.50–7.10 (m, 3, C_4, C_5, C_6 H's), 3.24 (dd, 1, $J_{C_{1a}-C_{1x}}$ = 8 Hz, $J_{C_{1a}-C_{1y}}$ = 7 Hz, C_{1a} H), 2.23 (dd, 1, $J_{C_{1x}-C_{1a}}$ = 8 Hz, $J_{C_{1x}-C_{1y}}$ = 7 Hz, C_1 H_x), 1.73 (t, 1, $J_{C_{1y}-C_{1x}}$ = $J_{C_{1y}-C_{1a}}$ = 7 Hz, C_1 H_y).

Anal. Calcd for $C_{10}H_7ClOS$: C, 57.00; H, 3.36; Cl, 16.83. Found: C, 57.25; H, 3.33; Cl, 16.80.

Using the same procedure as above, *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one[1] (1.00 g, 4.05 mmol) and triethylamine (3.50 ml, 25 mmol) in $CHCl_3$ (20 ml) gave after recrystallization from 60% ethanol 0.80 g (95%) of **28**, mp 61–62°. A mixture melting point with the above sample was not depressed and the ir and nmr spectra of both samples were identical.

Method B.—A mixture of 5-acetoxy-2,4-dichloro-2,3-dihydro-1-benzothiepin (1.00 g, 3.46 mmol), KOH (1.00 g, 18 mmol), and 95% ethanol (35 ml) was heated at 55° for 10 min. The excess KOH was removed by filtration, $CHCl_3$ (60 ml) was added, and the organic layer was washed with 10% HCl and H_2O and dried ($MgSO_4$). After the solvent was removed, the residual oil solidified upon addition of ice water and recrystallization from 60% ethanol gave 0.70 g (96%) of **28**, mp 61–62°. The ir and nmr spectra of this sample were identical with those of the above sample.

Method C.—Using the quantities and employing the reaction conditions listed in Table II, the reactions of **27** with base were quenched with 10% HCl. The organic layer was washed with H_2O, separated, and dried ($MgSO_4$). Analysis of the reaction mixture by nmr ($CDCl_3$) was performed on the residual oil which remained after removal of the solvent under vacuum.

7a-Chlorocyclopropa[*b*][1]benzothiopyran-7-one 2,2-Dioxide (31).—After a solution of 7a-chlorocyclopropa[*b*][1]benzothiopyran-7-one (0.68 g, 3.18 mmol) in $CHCl_3$ (10 ml) was added over a 15-min period to a stirred solution of *m*-chloroperbenzoic acid (1.26 g, 7.31 mmol) in $CHCl_3$ (15 ml) maintained at −10 to −16°, the reaction mixture was allowed to warm to room temperature and kept overnight at ambient temperature. *m*-Chlorobenzoic acid was removed by filtration, and the filtrate was washed with 10% Na_2CO_3 solution, dried ($MgSO_4$), and filtered. The solvent was removed and recrystallization of the residue from 95% ethanol gave 0.55 g (71%) of 7a-chlorocyclopropa[*b*][1]benzothiopyran-7-one 2,2-dioxide: mp 176.5–178°; ir (KBr) 1695 (>C=O), 1305, 1155 cm^{-1} (>SO_2); nmr ($CDCl_3$)[19] δ 8.20–7.75 (m, 4, aromatic H's), 3.82 (dd, 1, $J_{C_{1a}-C_{1x}}$ = 8 Hz, $J_{C_{1a}-C_{1y}}$ = 8.5 Hz, C_{1a} H), 2.31 [dd, 1+ (overlap with 1y), $J_{C_{1x}-C_{1a}}$ = 8 Hz, $J_{C_{1x}-C_{1y}}$ = 11.5 Hz, C_1 H_x), 2.16 [dd, 1+ (overlap with 1x), $J_{C_{1y}-C_{1a}}$ = 8.5 Hz, $J_{C_{1y}-C_{1x}}$ = 11.5 Hz, C_1 H_y).

Anal. Calcd for $C_{10}H_7ClO_3S$: C, 49.49; H, 2.91; Cl, 14.61; O, 19.78. Found: C, 49.50; H, 2.76; Cl, 14.94; O, 19.88.

7a-Bromocyclopropa[*b*][1]benzothiopyran-7-one (30).—A solution obtained by the addition of triethylamine (0.70 ml, 5 mmol) to *trans*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one[1] (200 mg, 0.70 mmol) in $CHCl_3$ (10 ml) was kept at room temperature for 17 min and neutralized with 10% HCl, and the organic layer was separated, washed with H_2O, and dried ($MgSO_4$). The solvent was removed and gave 168 mg (96%) of 7a-bromocyclopropa[*b*][1]benzothiopyran-7-one as a red oil: ir (neat) 3045 (w), 1685 (s, >C=O), 1590 (s), 1140 (m), 935 (s), 740 cm^{-1} (s); nmr ($CDCl_3$) δ 8.07–7.90 (m, 1, C_3 H), 7.50–7.10 (m, 3, C_4, C_5, C_6 H's), 3.26 (dd, 1, $J_{C_{1a}-C_{1x}}$ = 8 Hz, $J_{C_{1a}-C_{1y}}$ = 7 Hz, C_{1a} H), 2.25 (dd, 1, $J_{C_{1x}-C_{1a}}$ = 8 Hz, $J_{C_{1x}-C_{1y}}$ = 7.5 Hz, C_1 H_x), 1.79 (t, 1, $J_{C_{1y}-C_{1x}}$ = $J_{C_{1y}-C_{1a}}$ = 7 Hz, C_1H_y); mass spectrum (70 eV) *m/e* (rel intensity) 256 (20), 254 (20) [254/256 intensity ratio 0.97], 175 (100), 147 (100), 108 (32), 103 (20).

Thin layer chromatography of the red oil using benzene and benzene–ethanol (17:3) as eluents showed only one component present. Although **30** was obtained as a low-melting solid, mp 39–42°, elemental analysis was performed on the sulfone derivative (see below).

Compound **30** was also prepared from *cis*-4-bromo-2-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one[1] using the above procedure.

7a-Bromocyclopropa[*b*][1]benzothiopyran-7-one 2,2-Dioxide (32).—Using the procedure described for the preparation of **31**, the oxidation of 7a-bromocyclopropa[*b*][1]benzothiopyran-7-one (0.55 g, 2.16 mmol) with *m*-chloroperbenzoic acid (0.85 g, 4.97 mmol) gave, after crystallization from 95% ethanol, 0.60 g (97%) of 7a-bromocyclopropa[*b*][1]benzothiopyran-7-one 2,2-dioxide: mp 187.5–189.5°; ir (KBr) 1690 (>C=O), 1300 and 1150 cm^{-1} (>SO_2); nmr (DMSO-d_6),[19] δ 8.05 (s, 4, aromatic H's), 4.97 (t, 1, *J* = 8 Hz, C_{1a} H), 2.55 (m, 2, methylene bridge hydrogens, C_1 H's, appear in the same region as the solvent; subtracting the contribution of the solvent gave the correct integration for 2 H's).

Anal. Calcd for $C_{10}H_7BrO_3S$: C, 41.83; H, 2.46; Br, 27.83. Found: C, 41.50; H, 2.41; Br, 27.68.

5-Acetoxy-2,4-dichloro-2,3-dihydro-1-benzothiepin (34).—A solution of *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one[1] (1.00 g, 4.05 mmol), acetic anhydride (25 ml), and pyridine (4 ml) was allowed to stand at room temperature for 90 min, warmed on a steam bath for 30 min, cooled, and poured onto crushed ice. The resulting oil was extracted into $CHCl_3$ (60 ml); the extract was neutralized with 10% $NaHCO_3$ solution, washed with H_2O, and dried (Na_2SO_4). The solvent was removed under vacuum and gave 0.85 g (75%) of 5-acetoxy-2,4-dichloro-2,3-dihydro-1-benzothiepin as a reddish oil: ir (neat) 3065 (w), 1775 (s, >C=O), 1645 (m), 1370 (m), 1185 (broad, strong), 940 (m), 755 cm^{-1} (s); nmr ($CDCl_3$) δ 7.72–7.22 (m, 4, aromatic H's), 5.97 (dd, 1, $J_{C_2-C_{3a}}$ = 5.5 Hz, $J_{C_2-C_{3b}}$ = 11 Hz, –SCHCl–), 3.11 (dd, 1, $J_{C_{3a}-C_2}$ = 5.5 Hz, $J_{C_{3a}-C_{3b}}$ = 14.5 Hz, –SCHClC$H_a$$H_b$–), 2.68 (dd, 1, $J_{C_{3b}-C_2}$ = 11 Hz, $J_{C_{3b}-C_{3a}}$ = 14.5 Hz, –SCHClC$H_a$$H_b$–); mass spectrum (70 eV) *m/e* (rel intensity) 289 (2), 254 (3), 212 (16), 185 (100), 176 (17), 164 (17), 148 (40).

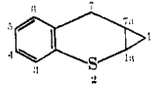
Thin layer chromatography of this oil using benzene, benzene–ethanol (17:3), and $CHCl_3$ as eluents indicated only one component. Elemental analysis was performed on the corresponding sulfone (see below).

5-Acetoxy-2,4-dichloro-2,3-dihydro-1-benzothiepin 1,1-Dioxide (35). Method A.—Employing the procedure described for the preparation of **31**, the oxidation of 5-acetoxy-2,4-dichloro-2,3-dihydro-1-benzothiepin (0.65 g, 2.24 mmol) with *m*-chloroperbenzoic acid (1.15 g, 6.67 mmol) in $CHCl_3$ (12 ml) gave, after crystallization from 95% ethanol, 0.31 g (41%) of 5-acetoxy-2,4-dichloro-2,3-dihydro-1-benzothiepin 1,1-dioxide: mp 147–148°; ir (KBr) 1770 (>C=O), 1330, and 1130 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.13–7.98 (m, 1, C_9 H), 7.68–7.30 (m, 3, C_6, C_7, C_8 H's), 5.30 (dd, 1, $J_{C_2-C_{3a}}$ = 5.5 Hz, $J_{C_2-C_{3b}}$ = 9 Hz, –SO_2CHCl–), 3.26 [dd, 1+ (overlaps with C_{3b} H), $J_{C_{3a}-C_2}$ = 5.5 Hz, $J_{C_{3a}-C_{3b}}$ = 14.5 Hz, –SO_2CHClC$H_a$$H_b$–], 2.94 [dd, 1+ (overlaps with C_{3a} H), $J_{C_{3b}-C_2}$ = 9 Hz, $J_{C_{3b}-C_{3a}}$ = 15 Hz, –SO_2CHClC$H_a$$H_b$–], 2.28 (s, 3, –$O_2CCH_3$).

Anal. Calcd for $C_{12}H_{10}Cl_2O_4S$: C, 44.88; H, 3.14; Cl, 22.08. Found: C, 44.57; H, 3.28; Cl, 22.33.

Method B.—A solution of *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide[1] (0.40 g, 1.43 mmol), acetic anhydride (18 ml), and pyridine (4 ml) was allowed to stand at room temperature for 50 min and the resulting yellow solution was poured onto ice. An oil separated, slowly solidified, and was collected, and recrystallization from 95% ethanol gave 0.40 g (90%) of **35**, mp 147–148.5°.

(19) For the numbering of **28** and related compounds see A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd ed, American Chemical Society, Washington, D. C., 1960, p 275.



In a second experiment *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide[1] (0.20 g, 0.72 mmol), acetic anhydride (12 ml), and pyridine (3 ml) were processed as above and gave 0.9 g (85%) of **35**, mp 147–148°. The ir and nmr spectra of these two samples were identical with those of **35** from method A.

5-Acetoxy-4-chloro-2,3-dihydro-1-benzothiepin 1,1-Dioxide (37).—A solution of 4-chloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide[1] (0.50 g, 2.04 mmol) in acetic anhydride (15 ml) and pyridine (4 ml) was allowed to stand at room temperature for 9 hr and poured onto crushed ice. An oil separated and slowly solidified upon stirring. Recrystallization of the solid from 95% ethanol gave 0.46 g (80%) of 5-acetoxy-4-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide: mp 147.5–149°; ir (KBr) 1770 (>C=O), 1305, and 1120 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.27–8.10 (m, 1, C_9 H), 7.78–7.33 (m, 3, C_6, C_7, C_8 H's), 3.85 (t, 2, J = 7 Hz, $-SO_2CH_aH_bCH_2-$), 2.94 (t, 2, J = 7 Hz, $-SO_2CH_2-CH_2-$), 2.30 (s, 3, $-O_2CCH_3$).

Anal. Calcd for $C_{12}H_{11}ClO_4S$: C, 50.27; H, 3.87; Cl, 12.37. Found: C, 50.36; H, 3.93; Cl, 12.21.

5-Acetoxy-4-bromo-2,3-dihydro-1-benzothiepin 1,1-Dioxide (38).—Using the preceding procedure 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide[1] (1.00 g, 3.50 mmol), acetic anhydride (20 ml), and pyridine (4 ml) were allowed to react at room temperature for 12 hr and gave, after recrystallization from 95% ethanol, 0.77 g (66%) of 5-acetoxy-4-bromo-2,3-dihydro-1-benzothiepin 1,1-dioxide: mp 161–162°; ir (KBr) 1775 (>C=O), 1640 (strong), 1300, 1170, and 1120 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.21–8.05 (m, 1, C_9 H), 7.73–7.40 (m, 3, C_6, C_7, C_8 H's), 3.83 (t, 2, J = 6 Hz, $-SO_2CH_2CH_2-$), 3.01 (t, 2, J = 6 Hz, $-SO_2CH_2CH_2-$), 2.29 (s, 3, $-O_2CCH_3$).

Anal. Calcd for $C_{12}H_{11}BrO_4S$: C, 43.52; H, 3.35; Br, 24.13. Found: C, 43.75; H, 3.38; Br, 24.11.

Reaction of 3,4-Dihydro-1-benzothiepin-5(2*H*)-one 1,1-Dioxide with Acetic Anhydride and Pyridine.—A solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide[18] (1.00 g), acetic anhydride (20 ml), and pyridine (5 ml) was warmed on a steam bath for 30 min and allowed to stand at room temperature for 28 hr. After the reaction solution was poured onto crushed ice and the colorless oil solidified, recrystallization of the solid gave 0.90 g (90%) of recovered starting material, mp 155–156°; its mixture melting point with starting material was not depressed and its ir spectrum was identical with that of an authentic sample.

When 3,4-dihydro-1-benzothiepin-5(2*H*)-one[18] and 4-bromo-3,4-dihydro-1-benzothiepin-5(2*H*)-one[1] were treated as above, no enol acetates were isolated, and only starting material was recovered.

4-Chloro-2,5-diacetoxy-2,3-dihydro-1-benzothiepin (39).—After a solution of 7a-chlorocyclopropa[*b*][1]benzothiopyran-7-one (1.30, 6.20 mmol) and a catalytic amount of *p*-toluenesulfonic acid in acetic anhydride (15 ml) was warmed on a steam bath for 5 min and allowed to remain at room temperature for 75 min, the reaction mixture was poured onto ice and the oil, which separated, slowly solidified to give a brown solid, mp 89–93°. Recrystallization of the brown solid from 95% ethanol gave 1.73 g (90%) of 4-chloro-2,5-diacetoxy-2,3-dihydro-1-benzothiepin: mp 104–105°; ir (neat) 3030 (w), 1775 (>C=O), 1750 (>C=O), 1650 (w), 1470 (s), 1200 (broad, strong), 1015 (s), 870 (m), 755 cm^{-1} (s); nmr ($CDCl_3$) δ 7.75–7.40 (m, 4, aromatic H's), 6.67 [dd, 1, $J_{C_2-C_{3a}}$ = 6 Hz, $J_{C_2-C_{3a}}$ = 11 Hz, $-SCH(OAc)CH_aH_b-$], 2.93 [dd, 1+ (overlaps with C_{3b} H), $J_{C_{3a}-C_2}$ = 6 Hz, $J_{C_{3a}-C_{3b}}$ = 14.5 Hz, $-SCH(OAc)CH_aH_b-$], 2.60 [dd, 1+ (overlaps with C_{3a} H), $J_{C_{3b}-C_2}$ = 11 Hz, $J_{C_{3b}-C_{3a}}$ = 14.5 Hz, $-SCH(OAc)CH_aH_b-$].

Anal. Calcd for $C_{14}H_{13}ClO_4S$: C, 53.76; H, 4.19; O, 20.46. Found: C, 53.48; H, 4.34; O, 20.48.

7a-Chloro-7-hydroxycyclopropa[*b*][1]benzothiopyran (41).—7a-Chlorocyclopropa[*b*][1]benzothiopyran-7-one (4.00 g, 19 mmol) in 95% ethanol (20 ml) was added over a 10-min period with stirring to a slurry of sodium borohydride (0.72 g, 20 mmol) in 95% ethanol (14 ml) and the reaction mixture was heated in an oil bath at 75° for 30 min and stirred at room temperature for 1 hr. The reaction mixture was poured onto an ice–hydrochloric acid mixture, the resulting oil was extracted into $CHCl_3$ (2 × 70 ml), and the extract was washed with H_2O and dried ($MgSO_4$). The solvent was evaporated under vacuum and gave 3.59 g (89%) of 7a-chloro-7-hydroxycyclopropa[*b*][1]benzothiopyran as a colorless oil: ir (neat) 3410 (broad, strong, –OH), 3070 (w), 1590 (m), 1129 (s), 1035 (s), 910 (m), 755 cm^{-1} (s); nmr ($CDCl_3$)[19] δ 7.83–7.09 (m, 4, aromatic H's), 5.02 (s, 1, –CHOH), 3.30 (s, 1, –CHOH), 2.60 (dd, 1, $J_{C_{1a}-C_{1x}}$ = 7 Hz, $J_{C_{1a}-C_{1y}}$ = 7.5 Hz, C_{1a} H), 1.26 [d, 2 (combined value of both C_{1x} H and C_{1y} H, a doublet with shoulders), $J_{C_{1x}-C_{1a}}$ = 7 Hz, C_1 H_x], 1.24 [d, 2 (combined value of both C_{1x} H and C_{1y} H), $J_{C_{1y}-C_{1a}}$ = 7.5 Hz, C_1 H_y]; mass spectrum (70 eV) *m/e* (rel intensity) 212 (38), 195 (52), 177 (67), 175 (42), 163 (38), 147 (100), 134 (48).

Thin layer chromatography of this oil using benzene and benzene–ethanol (9:1) as eluents indicated only one compound. Elemental analysis was performed on the corresponding sulfone (see below).

7a-Chloro-7-hydroxycyclopropa[*b*][1]benzothiopyran 2,2-Dioxide (42).—Using the procedure described for the preparation of **31**, the oxidation of 7a-chloro-7-hydroxycyclopropa[*b*][1]benzothiopyran (1.00 g, 5.0 mmol) with *m*-chloroperbenzoic acid (1.86 g, 11 mmol) in $CHCl_3$ (23 ml) over a 12-hr period gave, after recrystallization from 95% ethanol, 0.90 g (80%) of 7a-chloro-7-hydroxycyclopropa[*b*][1]benzothiopyran 2,2-dioxide: mp 122–123°; ir (KBr) 3440 (broad, strong, OH), 1300, 1160, and 1110 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 7.92–7.45 (m, 4, aromatic H's), 5.37 (d, 1, J = 5 Hz, –CHOH), 3.69 (d, 1, J = 5 Hz, –CHOH), 3.20 (dd, 1, $J_{C_{1a}-C_{1x}}$ = 6.5 Hz, $J_{C_{1a}-C_{1y}}$ = 9.0 Hz, C_{1a} H), 1.75–1.10 (m, 2, C_1 H_xH_y).

Anal. Calcd for $C_{10}H_9ClO_3S$: C, 49.08; H, 3.77; O, 19.61. Found: C, 49.12; H, 3.67; O, 19.57.

2-Acetoxy-4-chloro-2,3-dihydro-1-benzothiepin (43).—After a solution of 7a-chloro-7-hydroxycyclopropa[*b*][1]benzothiopyran (1.00 g, 4.70 mmol) and *p*-toluenesulfonic acid (0.85 g, 4.75 mmol) in acetic anhydride (10 ml) was warmed on a steam bath for 10 min and cooled, the reaction mixture was poured onto crushed ice and the oil was extracted with $CHCl_3$ (35 ml). The $CHCl_3$ extract was washed with 5% $NaHCO_3$ solution and H_2O and dried ($MgSO_4$) and, after the solvent was removed under vacuum, gave 1.00 g (84%) of 2-acetoxy-4-chloro-2,3-dihydro-1-benzothiepin as a yellow oil: ir (neat) 3060 (w), 1750 (>C=O), 1635 (m), 1730 (m), 1220 (s), 950 (m), 750 cm^{-1} (m); nmr ($CDCl_3$) δ 7.72–7.10 (m, 4, aromatic H's), 6.86 (s, 1, C_5 H), 6.52 (dd, 1, $J_{C_2-C_{3a}}$ = 7 Hz, $J_{C_2-C_{3b}}$ = 9 Hz, $-SCHOAc$), 2.80 [d, 2 (overlap of C_{3a} H and C_{3b} H), J = 7 Hz, $-SCH(OAc)CH_aH_b-$], 2.78 [d, 2 (overlap of C_{3a} H and C_{3b} H), J = 9 Hz, $-SCH(OA)-CH_aH_b-$], 2.04 (s, 3, $-O_2CCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 254 (4.1), 193 (39), 175 (19), 167 (19), 158 (19), 145 (100), 133 (24).

Elemental analysis was performed on the sulfone derivative (see following experiment).

2-Acetoxy-4-chloro-2,3-dihydro-1-benzothiepin 1,1-Dioxide (44).—Employing the procedure described for the preparation of **31**, the oxidation of 2-acetoxy-4-chloro-2,3-dihydro-1-benzothiepin (0.75 g, 2.95 mmol) with *m*-chloroperbenzoic acid (1.17 g, 6.78 mmol), after reaction overnight, gave after crystallization from 95% ethanol 0.65 g (82%) of 2-acetoxy-4-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide: mp 163–165°; ir (KBr) 1770 (>C=O), 1375, 1300, 1200, 1150 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.13–8.08 (m, 1, C_9 H), 7.83–7.31 (m, 3, C_6, C_7, C_8 H's), 6.98 (s, 1, C_5 H), 6.19 [t, 1, J = 7 Hz, $-SO_2CH(OAc)CH_2-$], 3.22 [d, 2, J = 7 Hz, $-SO_2CH(OAc)CH_2-$], 2.08 (s, 3, O_2CCH_3).

Anal. Calcd for $C_{12}H_{11}ClO_4S$: C, 50.26; H, 3.86; O, 22.32. Found: C, 50.43; H, 3.90; O, 22.16.

2,4-Dichloro-2,3-dihydro-1-benzothiepin (45).—HCl gas was bubbled into a solution of 7a-chloro-7-hydroxycyclopropa[*b*][1]benzothiopyran (1.00 g, 4.72 mmol) in $CHCl_3$ (5 ml) for 5 min at room temperature. After addition of $CHCl_3$ (15 ml) to the reaction mixture, the excess HCl was removed from the solution under a stream of nitrogen and the $CHCl_3$ solution was dried ($MgSO_4$). The solvent was removed under vacuum and gave 1.00 g (92%) of 2,4-dichloro-2,3-dihydro-1-benzothiepin: mp 55–57°; ir ($CHCl_3$) 3070 (w), 3010 (w), 1630 (s), 1470 (s), 1280 (m), 1174 (m), 1030 (s), 850 cm^{-1} (m); nmr ($CDCl_3$) δ 7.67–7.03 (m, 4, aromatic H's), 6.80 (s, 1, C_5 H), 5.75 (dd, 1, $J_{C_2-C_{3a}}$ = 6 Hz, $J_{C_2-C_{3b}}$ = 10 Hz, $-SCHClCH_aH_b-$), 3.03 [d, 2 (overlap of C_{3a} H and C_{3b} H), J = 6 Hz, $-SCHClCH_aH_b-$], 2.99 [d, 2 (overlap of C_{3a} H and C_{3b} H), J = 10 Hz, $-SCHClCH_aH_b-$]; mass spectrum (70 eV) *m/e* (rel intensity) 230 (11), 196 (38), 169 (100), 160 (51), 148 (64), 135 (64), 116 (83).

Attempts to recrystallize **45** from a variety of solvent systems led to an oil. Elemental analysis was obtained for its sulfone derivative (see following experiment).

2,4-Dichloro-2,3-dihydro-1-benzothiepin 1,1-Dioxide (46).—Using the procedure described for the preparation of **31**, the oxidation of 2,4-dichloro-2,3-dihydro-1-benzothiepin (0.50 g, 2.16 mmol) by *m*-chloroperbenzoic acid (0.86 g, 5.00 mmol) over

a 20-hr period gave, after recrystallization from 95% ethanol, 0.48 g (85%) of 2,4-dichloro-2,3-dihydro-1-benzothiepin 1,1-dioxide: mp 187–188.5°; ir ($CHCl_3$) 1635 (m), 1325, and 1150 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.38–8.24 (m, 1, C_9 H), 7.93–7.37 (m, 3, C_6, C_7, C_8 H's), 7.05 (s, 1, C_5 H), 5.22 (t, 1, J = 5 Hz, $-SO_2CHClCH_aH_b-$), 3.83 (dd, 1, $J_{C_{3a}-C_2}$ = 5 Hz, $J_{C_{3a}-C_{3b}}$ = 19 Hz, $-SOCHClCH_aH_b-$), 3.33 (dd, 1, $J_{C_{3b}-C_2}$ = 5.5 Hz, $J_{C_{3b}-C_{3a}}$ = 19 Hz, $-SO_2CHClCH_aH_b-$).

Anal. Calcd for $C_{10}H_8Cl_2O_2S$: C, 45.64; H, 3.06; Cl, 26.95; O, 12.16. Found: C, 45.51; H, 3.18; Cl, 26.67; O, 12.21.

Registry No.—**15**, 21609-70-1; **16**, 19373-31-0; **17**, 14171-33-6; **18**, 40322-44-9; **19**, 40322-45-0; **20**, 40322-46-1; **21**, 40322-47-2; **22**, 40322-48-3; **23**, 40322-49-4; **24**, 40322-50-7; **25**, 40322-51-8; **26**, 22710-97-0; **27a**, 40322-28-9; **27b**, 40322-29-0; **28**, 40322-30-3; **29a**, 40322-33-6; **29b**, 40322-34-7; **30**, 40322-58-5; **31**, 40322-59-6; **32**, 40322-60-9; **34**, 40322-61-0; **35**, 40322-62-1; **36** (X = Cl), 40322-63-2; **36** (X = Br), 21609-67-6; **37**, 40322-65-4; **38**, 40322-66-5; **39**, 40322-67-6; **41**, 40322-68-7; **42**, 40322-69-8; **43**, 40322-70-1; **44**, 40322-71-2; **45**, 40322-72-3; **46**, 40322-73-4; dimethylamine hydrochloride, 506-59-2; paraformaldehyde, 30525-89-4; isoamyl alcohol, 123-51-3; ethanol, 64-17-5; acetic acid, 64-19-7; formalin, 50-00-0; *tert*-butyl alcohol, 75-65-0; sodium hydroxide, 1310-73-2; benzaldehyde, 100-52-7; *p*-toluenesulfonic acid, 104-15-4; ozone, 10028-15-6; benzaldehyde 2,4-dinitrophenylhydrazone, 1157-84-2; ethyl formate, 109-94-4; morpholine, 110-91-8; triethylamine, 121-44-8; *m*-chloroperbenzoic acid, 937-14-14; acetic anhydride, 108-24-7; pyridine, 110-86-1; *cis*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide, 40322-31-4; *trans*-2,4-dichloro-3,4-dihydro-1-benzothiepin-5-(2*H*)-one 1,1-dioxide, 40322-32-5.

Synthesis of Thiabicyclo[2.2.2]octenes. Carbon-13 Nuclear Magnetic Resonance Spectra of Bicyclic Sulfides

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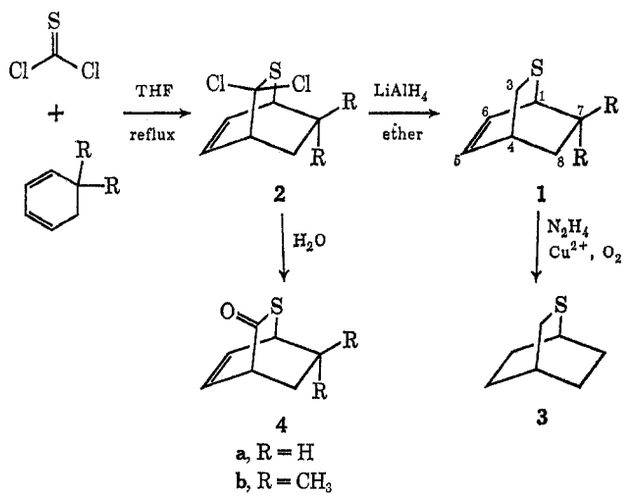
2-Thiabicyclo[2.2.2]oct-5-ene (**1a**) was synthesized by 1,4 addition of thiophosgene to 1,3-cyclohexadiene giving 3,3-dichloro-2-thiabicyclo[2.2.2]oct-5-ene (**2a**) followed by reduction with lithium aluminum hydride. 7,7-Dimethyl-2-thiabicyclo[2.2.2]oct-5-ene (**1b**) and 4,6,7,7-tetramethyl-2-thiabicyclo[2.2.2]oct-5-ene (**8**) were synthesized similarly from 5,5-dimethyl- and 1,3,5,5-tetramethyl-1,3-cyclohexadiene. Compound **1a** was characterized by diimide reduction to the known 2-thiabicyclo[2.2.2]octane which was shown not to be the photolysis product of 3-cyclohexenylmethanethiol (**5**) as previously reported. Compound **8** was characterized by oxidation to the sulfoxide **9** and sulfone **10**. Hydrolysis of the thiophosgene–cyclohexadiene adducts **2a**, **2b**, and **7** gave the corresponding δ-thiolactones **4a**, **4b**, and **12** (3-oxo-2-thiabicyclo[2.2.2]oct-5-enes). ^{13}C nmr was used to establish the structures of **1a**, **8**, **9**, **10**, and **12**.

Published synthetic approaches to the thiabicyclo[2.2.2]octene system have usually involved either cyclization of substituted cyclohexanes[1] or the cycloaddition of cyclohexadienes with thiocarbonyl compounds.[2] None of the reported syntheses is easily modified for the preparation of 2-thiabicyclo[2.2.2]-octene (**1a**) which we required for photochemical studies. In particular, reported examples of the latter method have involved substituted thiocarbonyl compounds (cyanothioformyl halides,[2a] perfluorinated thioketones,[2b] thiofluorenone,[2c] and thiobenzophenone[2d]) such that substituents are not easily replaced by hydrogen, and in any event have often proceeded in synthetically unattractive yields.

Middleton[2b] reported the cycloaddition of thiophosgene with cyclopentadiene to give 3,3-dichloro-2-thiabicyclo[2.2.1]hept-5-ene, and Johnson, Keiser, and Sharp[3] subsequently accomplished the reductive removal of the chlorine substituents, although only with difficulty and in low yield. The *S*-oxide of thiophosgene also undergoes cycloaddition with cyclopentadiene.[4] We have examined the reaction of thiophosgene with several cyclohexadienes and would like to report that this is a general route to the desired ring system, as well as to the saturated analog.

The reaction of cyclohexadiene with thiophosgene proceeded exothermically to give 3,3-dichloro-2-thiabicyclo[2.2.2]oct-5-ene (**2a**). Since the dichloride is moisture sensitive, reduction with lithium aluminum



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