Reaction of 20 with DDQ.—A solution of DDQ (71 mg, 0.31 mmol) and **19** (100 mg, 0.155 mm) in 20 ml of *o*-dichlorobenzene was refluxed overnight. The black solution was filtered and evaporated *in vacuo*. Chromatography on grade I neutral alumina yielded **20** (20 mg, 20%) upon benzene elution and **19** (65 mg, 65%) upon chloroform elution.

Attempted Reaction of 14 with DDQ in the Absence of Oxygen.—A thoroughly degassed solution of **14** (100 mg, 0.2 mm) and DDQ (150 mg, 0.6 mm) in *o*-dichlorobenzene (15 ml) was heated at 180° overnight in a sealed tube. The dark solution was filtered, reduced in volume (*in vacuo*), and chromatographed on neutral grade I alumina. Benzene elution yielded **14** (20 mg, 28% recovery) as the only isolable compound.

Reaction of 14 with Tetracyanoethylene in the Absence of Oxygen.—A degassed solution of **14** (150 mg, 0.3 mmol) and TCNE (96 mg, 0.75 mmol) in *o*-dichlorobenzene (10 ml) was heated in a sealed tube as above. Work-up yielded **14** (110 mg, 73%) as the only product.

Reaction of 20 with TCNE in the Absence of Air.—The above procedure carried out using **20** (150 mg, 0.23 mmol) and TCNE (74 mg, 0.58 mmol) resulted in the recovery of **20** (80 mg, 53%).

Reaction of 20 with DDQ in the Absence of Air.—Reaction of **20** (100 mg, 0.125 mmol) and DDQ (106 mg, 0.4 mmol) was carried out as above, resulting in the recovery of 28 mg of starting material.

Reaction of Pure 10 with Phosphorus Pentasulfide and Xylene.—A mixture of crystalline **10**[5] (200 mg), phosphorus pentasulfide (400 mg), and xylene (10 ml) was refluxed for 30 min (N_2). Alumina chromatography (benzene) yielded white needles of **20** (145 mg, 73%).

Oxidation of Pure 10 with DDQ in the Presence of Air.—A solution of **10** (100 mg) and DDQ (70 mg) in benzene (10 ml) was warmed for 2 min on a steam bath. Chromatography (silica, benzene) yielded diketone **19** (53 mg, 53%).

Air Oxidation of Pure 10.—A stream of air was passed through a suspension of **10** (50 mg) in xylene (20 ml) at room temperature for 2 hr with the exclusion of light. Chromatography (silica, benzene) yielded diketone **19** (22 mg, 44%).

Acknowledgment.—We thank the National Institutes of Health (for a Predoctoral Fellowship to M. A. Sprecker) and both the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial support of this work.

Registry No.—**1**, 36516-81-1; **10**, 41947-66-4; **13**, 3867-56-9; **14**, 41947-68-6; **18**, 41947-69-7; **19**, 41947-70-0; **20**, 42080-44-4; dibenzoylacetylene, 1087-09-8.

Seven-Membered Heterocycles. VII. The Synthesis and Properties of 1-Benzothiepin and Its Chlorinated Derivatives[1a,b]

VINCENT J. TRAYNELIS,* YOICHIRO YOSHIKAWA,[1c] JOHN C. SIH,[1c] AND LARKEY J. MILLER

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

JOEL R. LIVINGSTON, JR.[1d]

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received June 8, 1973

The reaction of 2,3-dihydro-1-benzothiepin (**7**) and sulfuryl chloride at low temperatures gave approximately equal amounts of *cis*- (**10**) and *trans*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin (**11**), characterized as their corresponding sulfones **12** and **13**, respectively. Chromatography of *cis*-**12** or reaction with KOH produced 5-chloro-2,3-dihydro-1-benzothiepin (**14**). Elimination reactions and nmr spectra were used to assign stereochemistry. When **7** was treated with 1 or 2 equiv of *N*-chlorosuccinimide, 2-chloro- (**8**) or 2,2-dichloro-2,3-dihydro-1-benzothiepins (**19**) were formed and converted to their sulfones **18** and **20**, respectively. An explanation for the different outcome of these two reactions is presented. The reaction of **8**, **19**, or 2,4-dichloro-2,3-dihydro-1-benzothiepin (**24**) with strong base gave 1-benzothiepin (**9**), 2-chloro-1-benzothiepin (**27**), and 4-chloro-1-benzothiepin (**28**). All of these compounds decomposed slowly at room temperature with extrusion of sulfur and formation of naphthalene. The 1-benzothiepins were oxidized to their corresponding sulfones **25**, **31**, and **32**, which were also prepared by dihydrochlorination of the α-chloro sulfones **18**, **20**, and 2,4-dichloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**33**). The thermal stability, mass spectra, and nmr spectra are discussed for both the 1-benzothiepins and their sulfones. The structure of these compounds appears to contain a puckered thiepin ring.

Several literature reports[2-4] have appeared in recent years which described the isolation of substituted 1-benzothiepins **1**–**6**. Most of these compounds **1**–**4**[2,3] were enol derivatives in which the parent enol preferentially tautomerizes to the keto structure. One exception is **6**,[4] obtained by mild hydrolysis of **5**, which exists in the enol form, most likely owing to intramolecular H bonding with the adjacent methoxycarbonyl group. These 1-benzothiepin derivatives appear to be stable at room temperature but extrude sulfur at elevated temperatures.

In this paper we wish to report the successful synthesis of the parent heterocycle 1-benzothiepin (**9**) and some of its chlorinated derivatives and their subsequent conversion to the corresponding 1-benzothiepin 1,1-dioxides. These synthetic approaches reflect a general method for producing this class of condensed thiepins.

The key precursor in these synthetic schemes was 2-chloro-2,3-dihydro-1-benzothiepin (**8**). In a previous publication[5] we examined the use of sulfuryl chloride for the α-chlorination[6] of 2,3-dihydro-1-benzothiepin (**7**). When these reactants were refluxed in petroleum ether (bp 30–60°) and $NaHCO_3$, the products isolated were sulfur (3–5%), naphthalene (5–10%), and unidentified chlorinated compounds. The origin of sulfur

(1) (a) For part VI in this series see V. J. Traynelis, J. C. Sih, and D. M. Borgnaes, *J. Org. Chem.*, **38**, 2629 (1973). (b) Presented in part before the Organic Division at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, and at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970. (c) Abstracted from a portion of the Ph.D. Dissertation submitted by Y. Y. in May 1973 and by J. C. S. in Dec 1971 at West Virginia University. (d) Abstracted from a portion of the Ph.D. Dissertation submitted by J. R. L., Jr., in March 1962 at the University of Notre Dame.

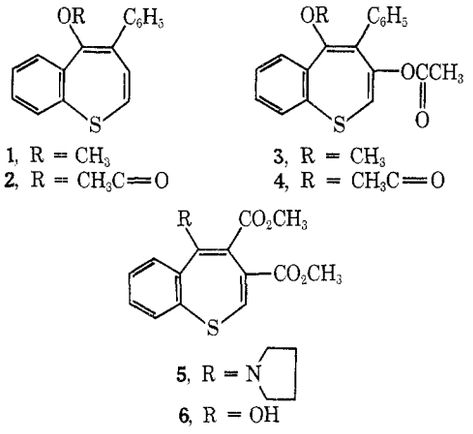
(2) H. Hofmann and H. Westernacher, *Chem. Ber.*, **102**, 205 (1969).

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

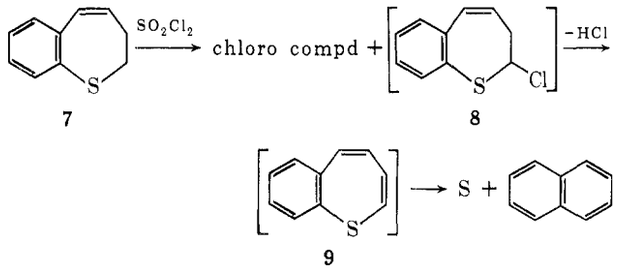
(4) D. N. Reinhoudt and C. G. Kourvenhoven, *Chem. Commun.*, 1233 (1972).

(5) V. J. Traynelis and J. R. Livingston, Jr., *J. Org. Chem.*, **29**, 1092 (1964).

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



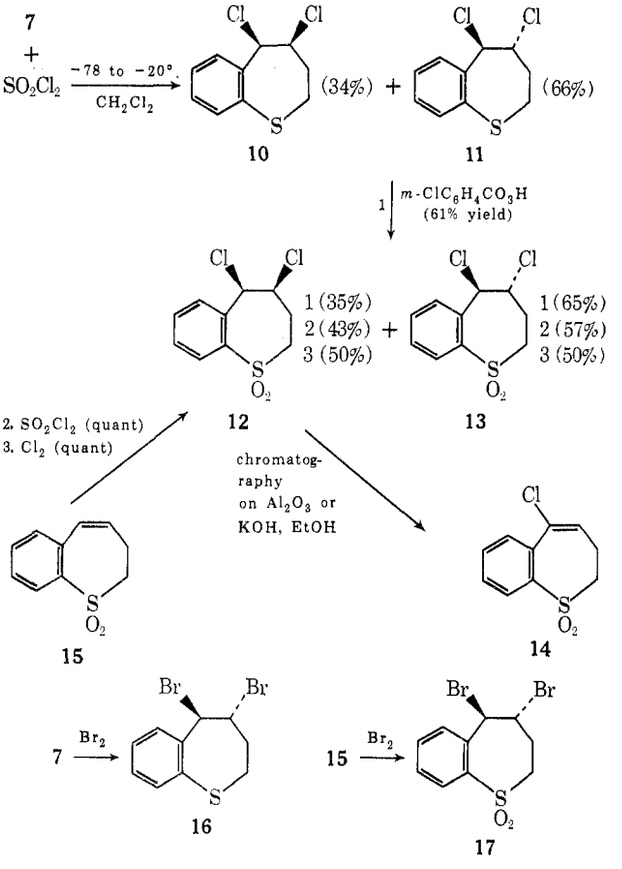
and naphthalene was rationalized by α-chlorination of **7** to give **8**, which lost hydrogen chloride to form 1-



benzothiepin (**9**), and subsequent sulfur extrusion in **9** gave sulfur and naphthalene.

The reaction of **7** and sulfuryl chloride was repeated, in which the reagents were mixed at −78° and kept at −20° for 1 week. The major products obtained by this procedure were *cis*- and *trans*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin (**10** and **11**, respectively) in a ratio of 34:66 cis:trans (determined by nmr analysis). No evidence for the presence of naphthalene was observed. Since these dichloro adducts **10** and **11** were thermally sensitive, they were not separated but the mixture was converted to the corresponding sulfones **12** and **13** (ratio 35:65 cis:trans) for characterization and structural assignment. Column chromatography of the sulfone mixture led to the pure trans isomer **13**, but the cis isomer **12** lost hydrogen chloride and was converted to 5-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**14**). In an independent experiment **12** was exposed to prolonged column chromatography on alumina and gave 91% conversion to **14**. Separation of sulfones **12** and **13** was accomplished by fractional crystallization, and structural assignments for **12**, **13**, and **14** were based on proper elemental analysis and consistent ir and nmr spectra for each.

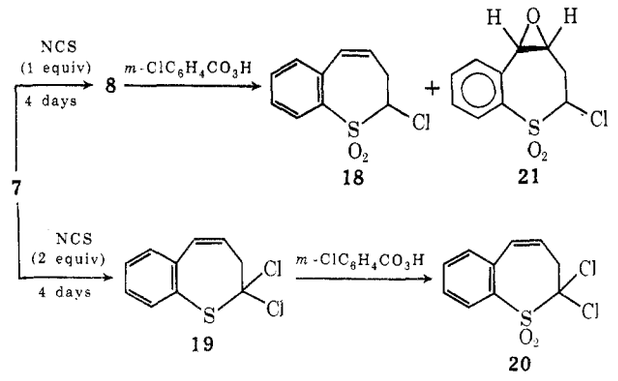
The facile elimination of hydrogen chloride from *cis*-**12** by KOH in ethanol in contrast to the absence of elimination from *trans*-**13** by KOH in ethanol favored the assignment of cis stereochemistry to **12**. These stereochemical assignments are further supported by the coupling pattern of the C_5 H, which was a singlet in *cis*-**10** and **12** (dihedral angle between the C_4 and C_5 hydrogens was approximately 90°) and a doublet in *trans*-**11** and **13** (J = 8 and 7 Hz, respectively, dihedral angle between the C_4 and C_5 hydrogens was approximately 0° or 180°). Similarly, the nmr spectra of



trans-4,5-dibromo-2,3,4,5-tetrahydro-1-benzothiepin (**16**) and its sulfone **17** showed a doublet for the C_5 H.

The reaction of **7** and sulfuryl chloride appears to be a simple addition of chlorine to the double bond. Similar cis/trans ratios of chlorine adducts **12** and **13** resulted from the reaction of sulfuryl chloride and chlorine with **15**. Thus the α-chlorination of **7** by sulfuryl chloride gave at best a very small amount of **8**[5] and does not provide a useful synthetic pathway to **8**.

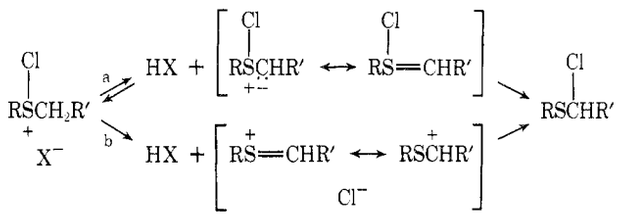
A second approach for the α-chlorination of **7** involved reaction with *N*-chlorosuccinimide (NCS).[7] When **7** and 1 or 2 equiv of NCS were allowed to react at room temperature for an extended period of time, 2-chloro- (**8**) or 2,2-dichloro-2,3-dihydro-1-benzothiepin (**19**), respectively, was formed in nearly quantitative yield. Compounds **8** and **19** were each characterized by their ir, nmr, and mass spectral characteristics; how-



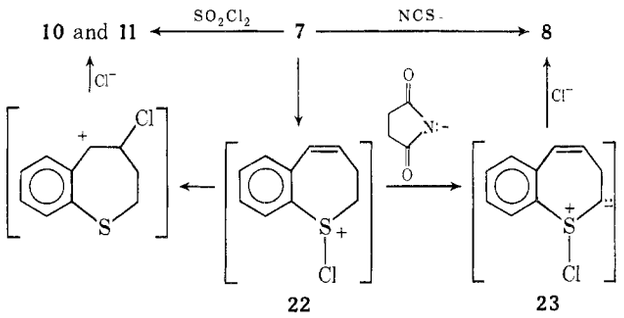
(7) D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969).

ever, both were thermally sensitive and were converted to their corresponding sulfones **18** and **20** for further characterization. Sulfones **18** and **20** showed spectral properties consistent with the assigned structures. A second product formed in the oxidation of **8** was assigned the epoxide structure **21** on the basis of elemental analysis and unique nmr and ir spectra.

The observed difference between NCS and sulfuryl chloride in the direction of chlorination of **7** can be rationalized *via* the mechanistic interpretation of Tuleen and Stevens.[7] Path a reflects abstraction of an acidic hydrogen to form an ylide which rearranges to an



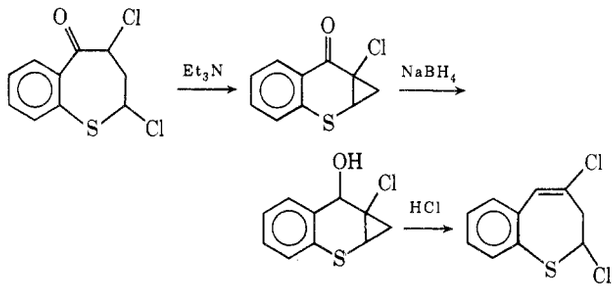
α-chloro sulfide, while path b represents an ionization to a thiacarbonium ion and chloride ion which recombine to produce the α-chloro sulfide. In the reaction of **7** with either NCS or sulfuryl chloride the initial intermediate proposed is the chlorosulfonium ion **22**. Evidence for this species was obtained by hydrolysis to 2,3-dihydro-1-benzothiepin 1-oxide.[8] Formation of α-chloro sulfide **8** with NCS parallels path a *via* ylide



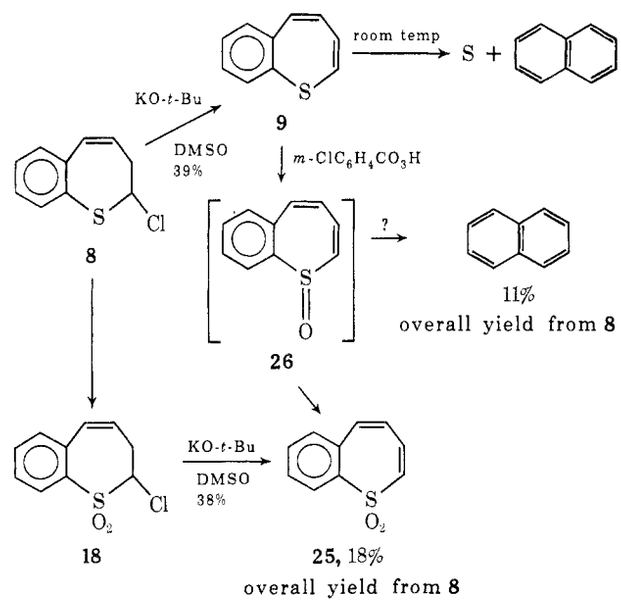
23 and may be attributed to the basic succinimidyl anion. However, chloride ion (the anion present in the sulfuryl chloride reaction) is not sufficiently basic to initiate path a and thus **22** should rearrange according to path b. However, in competition with the anticipated path b, which would ultimately form **8**, intermediate **22** can undergo a simple Cl^+ transfer to the olefinic center and lead to chlorine adducts **10** and **11**. Apparently the latter pathway, which may be facilitated by a transannular Cl^+ transfer, is preferred to the conversion of **22** to **8**.

Since 2-chloro-2,3-dihydro-1-benzothiepin (**8**) was now available, we were able to confirm its thermal conversion to sulfur and naphthalene.[5] Although **8** could be refluxed in pentane overnight without change, when **8** was refluxed in CCl_4 for 8 days, work-up led to the isolation of naphthalene (29%) and sulfur (14%). These reaction conditions appear more vigorous than those described for the reaction of **7** and sulfuryl chloride; however, in the earlier report[5] sodium bicarbonate was present during reflux of the reaction mixture.

A second avenue for the synthesis of 2-chloro-2,3-dihydro-1-benzothiepins has been described previously and entails the following ring contraction-ring expansion sequence illustrated with the synthesis of 2,4-dichloro-2,3-dihydro-1-benzothiepin (**24**).[1a]



The reaction of **8** with potassium *tert*-butoxide in DMSO at room temperature for 15 min followed by chromatography on alumina provided a 39% yield of 1-benzothiepin (**9**) as a yellow oil, mp ~15–19°. 1-Benzothiepin decomposed slowly at room temperature (about 3–4 days for complete decomposition) to produce sulfur and naphthalene; however, at Dry Ice temperatures **9** was stable for long periods of time. The structural assignment for **9** was based on the above extrusion reaction and nmr and mass spectral data (to be discussed later), and was confirmed by the oxidation of **9** with *m*-chloroperbenzoic acid to the known 1-benzothiepin 1,1-dioxide (**25**).[9] A second product isolated in the oxidation reaction was naphthalene. The source of naphthalene is most likely from decomposition of 1-benzothiepin, since 1-benzothiepin 1,1-dioxide is thermally quite stable even at temperatures over 200°;[9] however, one cannot exclude the oxidative intermediate, 1-benzothiepin 1-oxide (**26**), as a potential source of naphthalene *via* SO elimination.[10] A third method for



the synthesis of 1-benzothiepin 1,1-dioxide, which relates back to **8**, involved the dehydrochlorination of 2-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**18**).

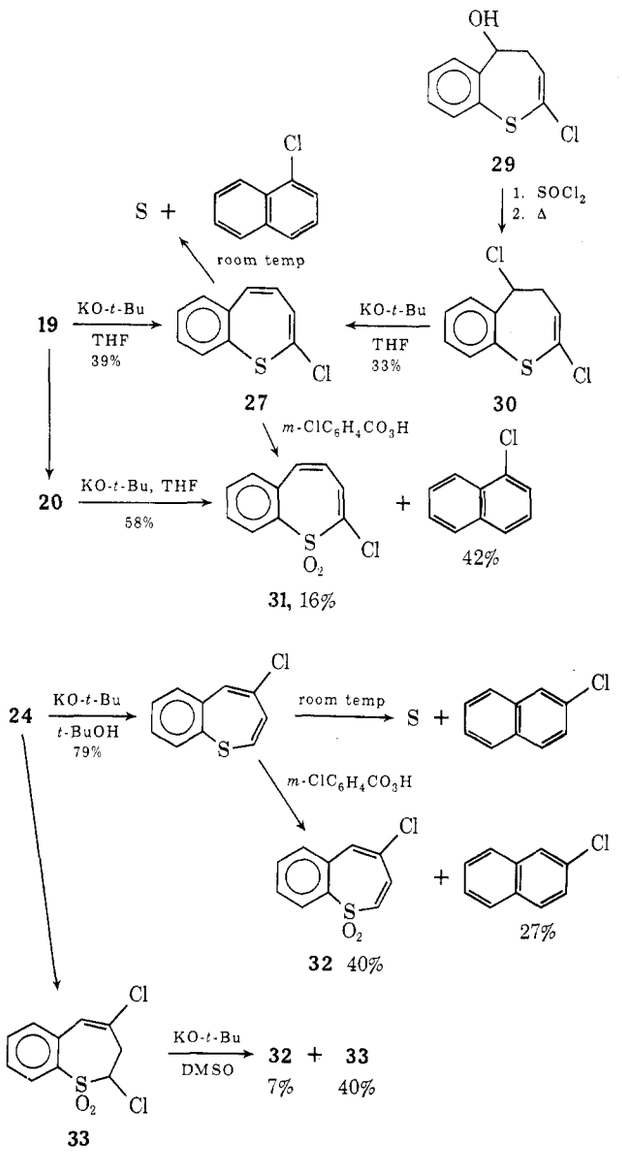
Similarly, the syntheses of 2-chloro-1-benzothiepin

(8) V. J. Traynelis, Y. Yoshikawa,, S. M. Tarka, and J. R. Livingston, Jr., *J. Org., Chem.*, **38**, 3986 (1973).

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

(10) V. J. Traynelis and D. M. Borgnaes, *J. Org. Chem.*, **37**, 3824 (1972).

(27) and 4-chloro-1-benzothiepin (28) were accomplished by treatment of 2,2-dichloro- (19) and 2,4-dichloro-2,3-dihydro-1-benzothiepin (24), respectively, with strong base. An alternate route to 27 was available by conversion of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin (29)[5] to the 2,5-dichloro derivative 30 followed by dehydrochlorination of 30 with potassium *tert*-butoxide in THF. Structural assignments for 27 and 28 followed the above approach for 9 and included thermal extrusion of sulfur with the formation of α- and β-chloronaphthalene, respectively, nmr and mass spectral data, and the oxidation of 27 and 28 to their corresponding sulfones 31 and 32. The physical and spectral properties of 31 were identical with those reported in the literature.[10] Again the oxidation reaction of the chloro-1-benzothiepins provided the corresponding chloronaphthalenes; however, the yields of the chloronaphthalenes were of such magnitude that one cannot rationalize their total origin from thermal decomposition of 27 or 28 alone. Since the 2- and 4-chloro-1-benzothiepins are also thermally stable, one must again consider the intermediate chloro-1-benzothiepin 1-oxides as potential precursors to the chloronaphthalenes *via* SO extrusion.



An alternate synthesis of 2-chloro- (31) and 4-chloro-1-benzothiepin 1,1-dioxide (32) was accomplished by treatment of 20 and 33 (synthesis described in a prior paper[1a]) with strong base. In the latter case the yield was extremely poor. Thus in summary of the synthetic procedures, the 2-chloro-2,3-dihydro-1-benzothiepins provide an excellent starting point for the synthesis of either 1-benzothiepins or their sulfone derivatives.

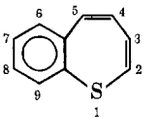
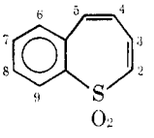
The thermal stability of the 1-benzothiepins 9, 27, and 28 is summarized in Table III. All compounds slowly decompose at room temperature to give sulfur and the corresponding naphthalene, while storage in the cold prolongs the lifetime of these compounds. When these 1-benzothiepins were heated to 60–80°, the sulfur extrusion reaction was very rapid and thus precludes use of elevated reaction temperatures in preparation or purification of these thiepins. Comparison of the thermal stability of the chloro-1-benzothiepins to the parent compound 9 suggests a slight increase in thermal stability when electron-withdrawing groups are present.[4] In contrast to the 1-benzothiepins, their respective sulfones are stable crystalline solids, which in some cases[9] can be heated to 300° for short periods of time. When decomposition does occur, the extrusion of sulfur dioxide and formation of naphthalene is at best minimal.[9]

The mass spectra of 9, 27, and 28 each showed an appreciable intensity for the parent molecule ion (56, 40, and 38%, respectively) and had the corresponding naphthalenes as the base peak. In view of the thermal instability of these 1-benzothiepins the high concentration of the parent molecule ion was somewhat surprising. The naphthalene radical ions can arise by sulfur extrusion of the 1-benzothiepin followed by ionization of the naphthalene or by ionization of the 1-benzothiepins followed by sulfur extrusion. Support for the presence of the latter pathway was found in 1-benzothiepin with the appearance of a metastable peak at *m/e* 102.4. Other important avenues of fragmentation included loss of Cl (in the chloro-1-benzothiepins and chloronaphthalenes) and the loss of CHS (from 1-benzothiepin) or CS and Cl (from the chloro-1-benzothiepins) to form the indenyl radical ion (*m/e* 115). The mass spectral fragmentation of the 1-benzothiepin sulfones 25, 31, and 32 was much simpler than that of the corresponding 1-benzothiepins and showed primarily the parent molecule ion peak and the respective naphthalene radical cations as the base peaks. In the chloro-1-benzothiepin dioxides there was also fragmentation entailing the loss of Cl. Since the 1-benzothiepin dioxides do not thermally extrude sulfur dioxide to any appreciable extent, the origin of the naphthalene base peaks requires sulfur dioxide loss from the parent molecule ion.

Table I shows a comparison of nmr spectral data for the known 1-benzothiepins and their sulfones. The thiepin ring protons appear downfield but are generally located in the olefinic region, except in a few cases where the C_5 hydrogen overlaps with aromatic hydrogens. These observations are consistent with the nonaromatic character and nonplanarity of the thiepin ring. The magnitude of the nmr coupling constants across the formal single bonds in fully unsaturated seven-membered cyclic compounds has been correlated to ring

TABLE I

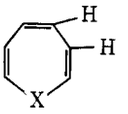
NMR DATA OF 1-BENZOTHIEPINS AND 1-BENZOTHIEPIN DIOXIDES

Substituent	δ C₂ H	C₃ H	C₄ H	C₆ H
				
1-Benzothiepin				
None	5.81	6.12–6.44		6.82–7.31[a]
2-Chloro		6.45	6.18	7.01
4-Chloro	5.78	6.15		6.8–7.15[a]
5-Methoxy-4-phenyl[b]	6.04	6.40		
5-Acetoxy-4-phenyl[b]	6.08	6.43		
3,5-Diacetoxy-4-phenyl[b]	6.0			
3-Acetoxy-5-methoxy-4-phenyl[b]	5.90			
3,4-Dimethoxycarbonyl-5-(*N*-pyrrolidino)[c]	7.00			
				
1-Benzothiepin 1,1-Dioxides				
None	6.56–7.00[d]			7.33
2-Chloro		7.10	6.70	7.56
4-Chloro	6.94	6.97		7.62–8.41[a]
3,5-Diacetoxy-4-phenyl[b]	6.75			

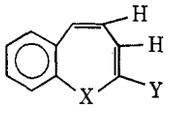
[a] These values represent the C_5 H and aromatic hydrogens. [b] See ref 3. [c] See ref 4. [d] These values represent C_2 H, C_3 H, and C_4 H.

TABLE II

COUPLING CONSTANTS IN UNSATURATED SEVEN-MEMBERED RINGS



X	J_{H-H}, Hz	Ref	Angular deviation,[a] deg Stern	Bow
CH_2[b]	5.6	*c*	40.5	36.5
SO_2[d]	7.0	*e*	22.8	44.6
$NSO_2C_6H_4Br$-*p*[f]	5.4	*g*	23	25[h]
C=O[i]	8.3	*h*	0	0
C=O, 2-chloro[j]	9.5	*h*	0	0



X	Y	J_{H-H}, Hz	Ref
CH_2	H	9.8	*k*
C=O	H	8.3	*h*
C=O	OH	9.8	*h*
S (**27**)	Cl	6.0	
SO_2 (**31**)	Cl	7.5	

[a] The angles are the deviation of the stern and bow of the boat from the plane of the remaining four carbon atoms. [b] M. Traetteberg, *J. Amer. Chem. Soc.*, **86**, 4265 (1964). [c] See ref 13. [d] H. L. Ammon, P. H. Watts, Jr., J. M. Stewart, and W. L. Mock, *J. Amer. Chem. Soc.*, **90**, 4501 (1968). [e] See ref 14. [f] I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *J. Amer. Chem. Soc.*, **90**, 5023 (1968). [g] This coupling constant was determined for carboethoxyazepine; see ref 13. [h] See ref 11. [i] K. Kimura, S. Suzuki, M. Kimura, and M. Kubo, *J. Chem. Phys.*, **27**, 320 (1957). [j] E. J. Forbes, M. J. Gregory, T. A. Hamor, and D. J. Watkin, *Chem. Commun.*, 114 (1966). [k] See ref 12.

planarity;[11,12] see Table II. The monocyclic systems in Table II show an increase in the coupling constant across the formal single bonds as the ring becomes more planar. The benzocycloheptatrienium ion (J = 9.8 Hz),[12] benzotropone (J = 8.3 Hz),[12] and benzotropolone ($J_{3,4}$ = 9.8 Hz)[11] are proposed as planar structures. In comparison, 2-chloro-1-benzothiepin (**27**) ($J_{3,4}$ = 6.0 Hz) and 2-chloro-1-benzothiepin 1,1-dioxide (**31**) ($J_{3,4}$ = 7.5 Hz) show a marked decrease in the coupling constants and resemble more closely the coupling constants for cycloheptatriene ($J_{2,3}$ = 5.6 Hz)[13] and thiepin 1,1-dioxide ($J_{3,4}$ = 7.0 Hz).[14] Thus one is led to the conclusion that **27** and **31** have a puckered heterocyclic ring most likely in a boat conformation as observed in thiepin 1,1-dioxide. Unfortunately, the nmr spectra (60 MHz) for 1-benzothiepin and its sulfone have a complex multiplet in the region of the C_3 H and C_4 H absorptions and thus precluded analysis of the coupling constants. However, by analogy to **27**, one would expect 1-benzothiepin to have a boat conformation for the thiepin ring moiety and approach the model used by Hofmann and coworkers[3] in their theoretical treatment of the structure of 1-benzothiepin. Final structural assignments await further physical measurements and X-ray analysis.

Experimental Section[15]

Reaction of 2,3-Dihydro-1-benzothiepin with Sulfuryl Chloride.—Sulfuryl chloride (1.67 g, 12.3 mmol) in CH_2Cl_2 (10 ml) was added over a 10-min period to a stirred solution of 2,3-dihydro-1-benzothiepin[9] (2.00 g, 12.3 mmol) in CH_2Cl_2 (15 ml) cooled to −78°. After the reaction mixture was stirred at −20° for 1 week, the solvent was removed and gave a mixture of *cis*- (**10**) and *trans*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin (**11**): nmr ($CDCl_3$) δ 7.70–7.08 (m, 4, aromatic H's), 5.90 [s, 1 (combined weight with C_5 H of the trans isomer), C_5 H, cis isomer], 5.50 [d, 1 (combined weight with C_5 H of the cis isomer), $J_{C_5-C_4}$ = 8 Hz, C_5 H, trans isomer], 4.65 [t, 1 (combined weight with C_4 H of the trans isomer), $J_{C_4-C_3}$ = 5 Hz, C_4 H, cis isomer], 4.34 [double t, 1 (combined weight with the C_4 H of the cis isomer), $J_{C_4-C_5}$ = 8, $J_{C_4-C_3}$ = 3.5 Hz, C_4 H trans isomer], 3.36–2.07 (m, 4, $-SCH_2CH_2-$, both isomers). Comparison of the C_5 H intensities for the cis and trans isomers showed a ratio of 34:66 cis:trans. These halides were thermally sensitive and thus were converted to their sulfones.

After the above mixture of isomers in $CHCl_3$ (10 ml) was added to *m*-chloroperbenzoic acid (5.0 g, 29 mmol) in $CHCl_3$ (30 ml) and the mixture was kept at 0° for 3 days, the reaction mixture was washed with 10% $NaHCO_3$ and H_2O and dried and the solvent was removed. The residue was chromatographed quickly from alumina (Alcoa F-20) using benzene as eluent and gave 2.0 g (61%) of a 35:65 mixture of *cis*- (**12**) and *trans*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide (**13**). The analysis of the mixture was by nmr using the intensities of the C_5 H peaks (δ 6.4 singlet for cis and 5.6 doublet for trans).

(11) D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *J. Amer. Chem. Soc.*, **91**, 5286 (1969).

(12) D. J. Bertelli, J. T. Gerig, and J. M. Herbelin, *J. Amer. Chem. Soc.*, **90**, 107 (1968).

(13) H. Gunther and H. H. Hinrichs, *Tetrahedron Lett.*, 787 (1966).

(14) W. L. Mock, M. P. Williamson, and S. M. Castellano, quoted in A. A. Bothner-By and E. Moser, *J. Amer. Chem. Soc.*, **90**, 2347 (1968).

(15) All melting points and boiling points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Ir spectra were determined on a Beckman IR-8 spectrophotometer, uv spectra were measured on a Bausch and Lomb 505 spectrophotometer, nmr spectra were recorded on a Varian Associates Model HA-60 or Model T-60 spectrometer, and the mass spectra were obtained on a Nuclide Corp. 12-90G high-resolution mass spectrometer.

Column chromatography of 1 g of the sulfone mixture on Al_2O_3 (A-540, 120 g) and elution with hexane–$CHCl_3$ (increasing concentration of $CHCl_3$ from 0 to 100%) gave first the trans isomer **13**, mp 165–166°, after two recrystallizations from $CHCl_3$–hexane. Sulfone **13** had identical nmr and ir spectra with those of trans dichloro sulfone **13** described below. The second fraction eluted was recrystallized three times from $CHCl_3$–hexane and was identified as 5-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**14**): mp 131–132°; ir ($CHCl_3$) 1320, 1310, 1155, 1140, 1120 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.19–8.02 (m, 1, C_9 H), 7.80–7.30 (m, 3, C_6, C_7, C_8 H's), 6.45 (t, 1, $J_{C_4-C_3}$ = 7.5 Hz, –CCl=CH–), 3.76 (t, 2, $J_{C_2-C_3}$ = 7.0 Hz, $-SO_2CH_2-$), 2.53 (two overlapping t, 2, $J_{C_3-C_4}$ = 7.5, $J_{C_3-C_2}$ = 7.0 Hz, $-SO_2CH_2CH_2-$).

Anal. Calcd for $C_{10}H_9ClO_2S$: C, 52.51; H, 3.97; Cl, 15.51. Found: C, 52.40; H, 3.75; Cl, 15.60.

Reaction of 2,3-Dihydro-1-benzothiepin 1,1-Dioxide with Sulfuryl Chloride.—After sulfuryl chloride (3.96 g, 29.7 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a stirred solution of 2,3-dihydro-1-benzothiepin 1,1-dioxide[9] (5.80 g, 29.7 mmol) in CH_2Cl_2 (30 ml) at −5 to −10°, the reaction mixture was stirred for 2 days and poured carefully into 5% $NaHCO_3$ solution, and the CH_2Cl_2 layer was separated, washed with H_2O, and dried ($MgSO_4$). The solvent was removed and left 7.6 g (99%) of a 43:57 mixture of *cis*- and *trans*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide. Analysis was made by nmr using the intensities of the C_5 H peaks (δ 6.4 singlet for cis and 5.6 doublet for trans).

Fractional crystallization of the mixture of isomers from $CHCl_3$–hexane gave pure *cis*-**12**, mp 169–170°, ir ($CHCl_3$) 1330, 1320, 1300, 1160, 1130, 1120 cm^{-1} (–SO_2–), nmr ($CDCl_3$) δ 8.15–7.23 (m, 4, aromatic H's), 6.41 (s, 1, C_5 H), 4.90 (m, 1, C_4 H), 3.47–2.14 (m, 4, $-SO_2CH_2CH_2-$), and pure *trans*-**13**, mp 165–166°, ir ($CHCl_3$), 1330, 1325, 1305, 1160, 1140, 1125 cm^{-1} (–SO_2–), nmr ($CDCl_3$) δ 8.28–8.10 (m, 1, C_9 H), 7.73–7.54 (m, 3, C_6, C_7, C_8 H's), 5.59 (d, 1, $J_{C_5-C_4}$ = 7.0 Hz, C_5 H), 4.70–4.48 (m, 1, C_4 H), 4.08–2.2 (m, 4, $-SO_2CH_2CH_2-$).

Anal. Calcd for $C_{10}H_{10}Cl_2O_2S$: C, 45.29; H, 3.80; Cl, 26.74. Found for cis isomer: C, 45.24; H, 3.91; Cl, 26.53. Found for trans isomer: C, 45.45; H, 3.66; Cl, 26.76.

Addition of Chlorine to 2,3-Dihydro-1 benzothiepin 1,1-Dioxide.—Chlorine gas was bubbled for 10 min into a solution of 2,3-dihydro-1-benzothiepin 1,1-dioxide[9] (257 mg, 1.32 mmol) in CH_2Cl_2 (5 ml) at room temperature and after 10 additional min the excess chlorine was removed under a stream of nitrogen. The solvent was evaporated and gave 352 mg (100%) of a white solid which was shown by nmr to be a 50:50 mixture of *cis*- and *trans*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide.

5-Chloro-2,3-dihydro-1-benzothiepin 1,1-Dioxide (14). Method A.—*cis*-4,5-Dichloro-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide (**12**, 100 mg, 0.38 mmol) was placed on an alumina column (A-540, 20 g) and washed with 250 ml of 1:1 $CHCl_3$–pentane. The recovered solid was starting material.

When **12** was allowed to remain on the column for approximately 9 days, elution from the column as described above gave 78 mg (91%) of crude 5-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide, mp 122–125°. Recrystallization from $CHCl_3$–pentane gave pure **14**, mp 130–131°, which had an nmr spectrum identical with that of the above sample of **14**.

Method B.—A solution of *cis*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide (160 mg, 0.60 mmol) and KOH (34 mg, 0.62 mmol) in 95% ethanol (18 ml) was stirred at room temperature for 1 hr and the reaction mixture was poured into H_2O (30 ml) and extracted with $CHCl_3$. After the $CHCl_3$ extract was washed with H_2O and dried ($MgSO_4$), the solvent was removed and gave 104 mg (76%) of crude **14**, mp 110–118°. Recrystallization from 95% ethanol gave pure **14**, mp 129–130°, which had an nmr spectrum identical with that of the above sample.

In a second experiment *trans*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide (160 mg, 0.60 mmol) and KOH (34 mg, 0.62 mmol) in ethanol (18 ml) after 2 hr at room temperature gave 131 mg (82%) of unreacted starting material, mp 163–164°, identified by its nmr.

***trans*-4,5-Dibromo-2,3,4,5-tetrahydro-1-benzothiepin (16).**[16]—Solid pyridinium hydrobromide perbromide[17] (9.95 g, 31 mmol) was added slowly to a solution of 2,3-dihydro-1-benzothiepin[5] (4.8 g, 30 mmol) in $CHCl_3$ (30 ml) at 5°. After the reaction mixture was stirred for 30 min at room temperature, washed with H_2O (50 ml) containing sodium thiosulfate, washed with H_2O, and dried ($MgSO_4$), the solvent was removed and the residue (8.13 g, 85%) was recrystallized from ether to give 7.1 g (75%) of *trans*-4,5-dibromo-2,3,4,5-tetrahydro-1-benzothiepin (**16**): mp 107–108°; nmr ($CDCl_3$) δ 7.58–7.08 (m, 4, aromatic H's), 5.60 (d, 1, J = 6 Hz, C_5 H), 4.81 (m, 1, C_4 H), 3.27–2.13 (m, 4, C_2 H's and C_3 H's).

Anal. Calcd for $C_{10}H_{10}Br_2S$: C, 37.29; H, 3.13; Br, 49.62. Found: C, 37.40; H, 3.46; Br, 49.39.

***trans*-4,5-Dibromo-2,3,4,5-tetrahydro-1-benzothiepin 1,1-Dioxide (17).**—The procedure described in the literature[9] was repeated and gave 83% *trans*-4,5-dibromo-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide (**17**): mp 197–199° (lit.[9] mp 195–196°); ir ($CHCl_3$) 1325, 1300, 1150, 1120 cm^{-1} (–SO_2–); nmr ($CDCl_3$) δ 8.40–8.07 (m, 1, C_9 H), 7.95–7.25 (m, 3, C_6, C_7, C_8 H's), 5.68 (d, 1, J = 5.5 Hz, C_5 H), 4.90 (d t, 1, $J_{C_4-C_5}$ = 5.5, $J_{C_4-C_3}$ = 2 Hz, C_4 H), 4.15–3.18 (m, 3, C_2 H's and C_3 H_b), 2.70–2.20 (m, 1, C_3 H_a).

2-Chloro-2,3-dihydro-1-benzothiepin (8).—After a mixture of *N*-chlorosuccinimide (5.0 g, 37.4 mmol), 2,3-dihydro-1-benzothiepin[5] (5.1 g, 31.5 mmol), and CCl_4 (40 ml) was stirred at ambient temperature for 4 days, the solid was removed by filtration and the solvent was removed under reduced pressure. The residue was exposed to high vacuum and gave 6.19 g (100%) of 2-chloro-2,3-dihydro-1-benzothiepin (**8**): ir (neat) 3030 (m), 2920 (m), 1710 (m), 1465 (m), 1430 (m), 1270 (w), 1190 (w), 1150 (w), 1055 (w), 930 (w), 825 (w), 765 (s), 740 (s), 720 (s), 685 (s), 670 cm^{-1} (s); nmr ($CDCl_3$) δ 7.70–7.53 (m, 1, C_9 H), 7.35–7.04 (m, 3, C_6, C_7, C_8 H's), 6.71 (d, 1, $J_{C_5-C_4}$ = 11 Hz, C_5 H), 6.07 (d t, 1, $J_{C_4-C_5}$ = 11, $J_{C_4-C_3}$ = 6.5 Hz, C_4 H), 5.62 (d d, 1, $J_{C_2-C_{3a}}$ = 5.3, $J_{C_2-C_{3b}}$ = 10 Hz, –SCHCl–), 2.93 [two d d, 2 (total weight for C_{3a} and C_{3b}), $J_{C_{3a}-C_2}$ = 5.3, $J_{C_{3a}-C_4}$ = 6.5, $J_{C_{3a}-C_{3b}}$ = 14 Hz, –SCHClC$\mathbf{H}_a\mathbf{H}_b$–], 2.50 [two d d, 2 (total weight for C_{3a} and C_{3b}), $J_{C_{3b}-C_2}$ = 10, $J_{C_{3b}-C_4}$ = 6.5, $J_{C_{3b}-C_{3a}}$ = 14 Hz, –SCHClC$\mathbf{H}_a\mathbf{H}_b$–]; mass spectrum (70 eV) *m/e* (rel intensity) 196 (4), 161 (31), 160 (43), 147 (29), 134 (100), 128 (71), 119 (29), 117 (27), 115 (31), 106 (34), 105 (36), 91 (77), 77 (44), 63 (21).

Completion of reaction was conveniently followed by nmr. Elemental analysis was performed on the corresponding sulfone (see following experiment).

2-Chloro-2,3-dihydro-1-benzothiepin 1,1-Dioxide (18).—2-Chloro-2,3-dihydro-1-benzothiepin (3.39 g, 17.2 mmol) prepared from the reaction of 2,3-dihydro-1-benzothiepin[5] (3.24 g, 20 mmol) and *N*-chlorosuccinimide (3.48 g, 26.2 mmol) was dissolved in $CHCl_3$ (10 ml) and the solution was added dropwise over 15 min to a stirred solution of *m*-chloroperbenzoic acid (8.63 g, 50 mmol) in $CHCl_3$ (40 ml) cooled to −20°. After the reaction mixture was warmed to room temperature and stirred for 1 day, the reaction mixture was filtered and the filtrate was washed with 10% Na_2CO_3 solution and H_2O and dried ($MgSO_4$). The solvent was evaporated and gave 3.44 g of a 55:45 mixture of 2-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**18**) and 2-chloro-4,5-oxido-2,3-dihydro-1-benzothiepin 1,1-dioxide (**21**). The analysis of the mixture was made by comparison of the intensities of the nmr peaks for the C_5 hydrogen in each compound. Fractional recrystallization from 95% ethanol provided 0.38 g (10%) of pure 2-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**18**): mp 114–115°; ir ($CHCl_3$) 1310, 1145, and 1120 cm^{-1} (–SO_2–); nmr ($CDCl_3$) δ 8.24–8.07 (m, 1, C_9 H), 7.76–7.24 (m, 3, C_6, C_7, C_8 H's), 6.66 (d t, 1, $J_{C_5-C_4}$ = 13, $J_{C_5-C_{3a,b}}$ = 1.8 Hz, C_5 H), 5.93 (d t, 1, $J_{C_4-C_5}$ = 13, $J_{C_4-C_{3a,b}}$ = 5 Hz, C_4 H), 5.13 (t, 1, J = 5 Hz, $-SO_2CHCl-$), 2.45 [two d t, 2 (combined weight for C_{3a} H and C_{3b} H), $J_{C_{3a}-C_4,C_2}$ = 5, $J_{C_{3a}-C_5}$ = 1.8, $J_{C_{3a}-C_{3b}}$ = 19 Hz, $-SO_2CHClC\mathbf{H}_a\mathbf{H}_b-$], 2.99 [two d t, 2 (combined weight for C_{3a} H and C_{3b} H), $J_{C_{3b}-C_4,C_2}$ = 5, $J_{C_{3b}-C_5}$ = 1.8, $J_{C_{3b}-C_{3a}}$ = 19 Hz, $-SO_2CHClCH_a\mathbf{H}_b-$]; mass spectrum (70 eV) *m/e* (rel intensity) 228 (46), 193 (64), 175 (25), 163 (18), 153 (95), 147 (50), 137 (54), 129 (41), 128 (100), 127 (57), 115 (25).

Anal. Calcd for $C_{10}H_9ClO_2S$: C, 52.51; H, 3.97; Cl, 15.51. Found: C, 52.85; H, 3.92; Cl, 15.37.

The second product from fractional crystallization with 95% ethanol was further purified by recrystallization from $CHCl_3$ and gave 0.32 g (8%) of 2-chloro-4,5-oxido-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide (**21**): mp 169.5–171°; ir ($CHCl_3$) 3030 (m), 1425 (m), 1330, 1150, 1120 (–SO_2–), 950 (w), 870 (w), 800 cm^{-1} (w); nmr ($CDCl_3$) δ 8.11–7.93 (m, 1, C_9 H), 7.80–7.40 (m, 3, C_6, C_7, C_8 H's), 5.03 (d d, 1, $J_{C_2-C_{3a}}$ = 2.5, $J_{C_2-C_{3b}}$ = 5.2 Hz, $-SO_2CHCl-$), 4.32 (d, 1, $J_{C_5-C_4}$ = 4.2 Hz, C_5 H), 3.71 (two d d, 1, $J_{C_4-C_5}$ = 4.2, $J_{C_4-C_{3a}}$ = 4.4, $J_{C_4-C_{3b}}$ = 9.0 Hz, C_4 H),

(16) R. F. Love, Ph.D. Dissertation, University of Notre Dame, 1960.
(17) L. F. Fieser, *J. Chem. Educ.*, **31**, 291 (1954).

2.83 (two d d, 1, $J_{C_{3a}-C_2}$ = 2.5, $J_{C_{3a}-C_4}$ = 4.4, $J_{C_{3a}-C_{3b}}$ = 15.6 Hz, $-SO_2CHClCH_aH_b-$), 1.68 (two d d, 1, $J_{C_{3b}-C_2}$ = 5.2, $J_{C_{3b}-C_4}$ = 9, $J_{C_{3b}-C_{3a}}$ = 15.6 Hz, $-SO_2CHClCH_aH_b-$).

Anal. Calcd for $C_{10}H_9ClO_3S$: C, 49.08; H, 3.71; Cl, 14.49; S, 13.10. Found: C, 49.09; H, 3.55; Cl, 14.62; S, 12.85.

The remainder of the product mixture showed the presence of olefin sulfone **18** and epoxide **21** and was not separated further.

2,2-Dichloro-2,3-dihydro-1-benzothiepin (19).—Using the procedure described above for the preparation of **8**, the mixture of 2,3-dihydro-1-benzothiepin[5] (4.86 g, 30 mmol) and *N*-chlorosuccinimide (9.6 g, 66 mmol) in CCl_4 (40 ml) was stirred with a Hershberg stirrer at room temperature for 4 days and afforded 6.8 (98%) of 2,2-dichloro-2,3-dihydro-1-benzothiepin (**19**) as a brown oil: ir (CCl_4) 3060 (w), 1740 (m), 1460 (m), 1425 (m), 1300 (w), 1230 (w), 1200 (w), 1150 (w), 1000 (w), 945 cm^{-1} (w); nmr (CCl_4) δ 7.67–7.08 (m, 4, aromatic H's), 6.90 (d, 1, $J_{C_5-C_4}$ = 11 Hz, C_5 H), 6.26 (d t, 1, $J_{C_4-C_5}$ = 11, $J_{C_4-C_3}$ = 7 Hz, C_4 H), 3.10 (d, 2, J = 7 Hz, $-SCCl_2CH_2-$); mass spectrum (70 eV) *m/e* (rel intensity) 230 (3), 194 (24), 162 (23), 160 (26), 159 (26), 147 (6), 134 (100), 127 (10), 126 (9), 115 (57). Elemental analysis was performed on the corresponding sulfone (see following experiment).

When the above reaction is performed with ordinary stirring, the reaction time is doubled.

2,2-Dichloro-2,3-dihydro-1-benzothiepin 1,1-Dioxide (20).—A solution of 2,2-dichloro-2,3-dihydro-1-benzothiepin (2.31 g, 10 mmol) in $CHCl_3$ (15 ml) was added over 10 min to a stirred solution of *m*-chloroperbenzoic acid (3.46 g, 20 mmol) in $CHCl_3$ (15 ml) maintained at −5° and the reaction mixture was stirred at room temperature overnight. The reaction mixture was processed as described in the preparation of **18** and gave, after recrystallization from $CHCl_3$–hexane, 1.16 g (44%) of 2,2-dichloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**20**): mp 164–165°; ir ($CHCl_3$) 1330, 1310, 1210, 1155, 1130 cm^{-1} ($-SO_2-$); nmr ($CDCl_3$) δ 8.33–8.13 (m, 1, C_9 H), 7.76–7.20 (m, 3, C_6, C_7, C_8 H's), 6.65 (d t, 1, $J_{C_5-C_4}$ = 13, $J_{C_5-C_3}$ = 2 Hz, C_5 H), 5.83 (d t, 1, $J_{C_4-C_5}$ = 11, $J_{C_4-C_3}$ = 5 Hz, C_4 H), 3.64 (d d, 2, $J_{C_3-C_4}$ = 5, $J_{C_3-C_5}$ = 2 Hz, $-SO_2CCl_2CH_2-$); mass spectrum (70 eV) *m/e* (rel intensity) 26.4 (19), 262 (26), 245 (7), 227 (16), 209 (24), 181 (33), 162 (42), 153 (100), 137 (59), 128 (56), 127 (53).

Anal. Calcd for $C_{10}H_8Cl_2O_2S$: C, 45.80; H, 2.69; Cl, 27.05. Found: C, 45.66; H, 2.92; Cl, 27.08.

1-Benzothiepin (9).—A solution of powdered potassium *tert*-butoxide (0.672 g, 6 mmol) in dimethyl sulfoxide (10 ml) was added in several portions to a solution of 2-chloro-2,3-dihydro-1-benzothiepin (0.985 g, 5 mmol) in dimethyl sulfoxide (10 ml) at room temperature. After the reaction mixture was stirred for 15 min at room temperature, the reddish-black solution was poured into H_2O (30 ml) and the aqueous solution was extracted with $CHCl_3$ (30 ml). The extract was washed with H_2O, dried ($MgSO_4$), and concentrated *in vacuo* (below room temperature). The residual heavy black oil (0.80 g) was chromatographed on alumina (A-540, 40 g) with Skelly F as the eluent and the combined yellow fractions gave 308 mg (38.5%) of 1-benzothiepin (**9**) as a yellow liquid: solidifies between 15 and 20°; ir ($CHCl_3$) 3060 (m), 3000 (s), 1575 (m), 1470 (s), 1430 (s), 1330 (s), 1290 (w), 1255 (s), 1120 (w), 1060 (m), 1030 (w), 940 (w), 875 (m), 665 cm^{-1} (s); nmr ($CDCl_3$) δ 7.31–6.82 (m, 5, aromatic H's and C_5 H), 6.44–6.12 (m, 2, C_4 H and C_3 H), 5.81 (d, 1, J = 8.5 Hz, C_2 H); mass spectrum (70 eV) *m/e* (rel intensity) 160 (56), 134 (12), 129 (22), 128 (100), 116 (16), 115 (40), 102 (7).

The work-up process must be performed rapidly to avoid thermal decomposition of 1-benzothiepin to naphthalene and sulfur.

1-Benzothiepin 1,1-Dioxide (25). Method A.—To a stirred solution of 2-chloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (**18**, 0.19 g, 0.83 mmol) in dimethyl sulfoxide (3 ml) was added at room temperature two portions of powdered potassium *tert*-butoxide (200 mg, 1.16 mmol). After the reaction mixture was stirred for 15 min at room temperature, the dark green solution was poured into H_2O (20 ml) and $CHCl_3$ (20 ml) and the $CHCl_3$ layer was separated, washed with H_2O, and dried ($MgSO_4$). The $CHCl_3$ was removed under reduced pressure and left 0.06 g (38%) of crude 1-benzothiepin 1,1-dioxide, mp 131–134°. Recrystallization of the crude product gave pure **25**: mp 140–141° (lit.[9] mp 140–141°); ir ($CHCl_3$) 3015 (w), 1610 (w), 1575 (w), 1545 (w), 1465 (w), 1335, 1305, 1160, 1150, 1120 ($-SO_2-$), 1060 (m), 785 (w), 680 cm^{-1} (w); nmr ($CDCl_3$) δ 8.27–8.07 (m, 1, C_9 H), 7.81–7.53 (m, 3, C_6, C_7, C_8 H's), 7.33 (d, 1, J = 13 Hz, C_5 H), 7.00–6.56 (m, 3, C_2 H, C_3 H, C_4 H); mass spectrum (70 eV) *m/e* (rel intensity) 192 (26), 163 (10), 149 (14), 147 (10), 129 (15), 128 (100), 115 (13), 102 (13). A mixture melting point with an authentic sample[9] of **25** was not depressed.

Method B.—Crude 1-benzothiepin obtained from the reaction of 2,3-dihydro-1-benzothiepin (5.0 g, 30.9 mmol) and *N*-chlorosuccinimide (4.6 g, 34.4 mmol) followed by dehydrochlorination with potassium *tert*-butoxide (3.7 g, 36 mmol) was dissolved in $CHCl_3$ (30 ml) and the solution was added over a 15-min period to a solution of *m*-chloroperbenzoic acid (12.0 g, 59.1 mmol) in $CHCl_3$ (20 ml) maintained at −50°. The reaction mixture was stirred at −50° for 30 min and allowed to remain at 0° for 3 days. After the reaction mixture was filtered and the solvent was removed, a quick chromatography on alumina of the black, viscous residue (6.1 g) with elution by benzene gave 2.9 g of a black paste. A second chromatography of the 2.9 g of black material on alumina (A-540, 90 g) gave, upon elution with $CHCl_3$–Skelly F (1:1 v/v) first 0.45 g (11% based on 2,3-dihydro-1-benzothiepin) of naphthalene, mp 70–73° (sublimed, mp 79–80°), ir and nmr identical with those of an authentic sample, and second 1.1 g (18% based on 2,3-dihydro-1-benzothiepin) of 1-benzothiepin 1,1-dioxide, mp 134–136°. Recrystallization of the crude product gave pure **25**, mp 140–141°. A mixture melting point with an authentic sample was not depressed and the ir and nmr spectra were identical with those of an authentic sample.

Pyrolysis of 2-Chloro-2,3-dihydro-1-benzothiepin.—A solution of 2-chloro-2,3-dihydro-1-benzothiepin (**8**) (1.5 g, 7.6 mmol) in CCl_4 (10 ml) was refluxed for 9 days, after which time the nmr spectrum of the reaction mixture showed the absence of **8**. The solvent was removed under reduced pressure and the residual dark oil (1.4 g) was chromatographed on alumina (A-540, 150 g), and elution with Skelly F gave 407 mg of a white solid. A second chromatography of the white solid on alumina (A-540, 50 g) and elution with Skelly F gave 33 mg (14%) of sulfur, mp 112–121°. Recrystallization from ethyl acetate afforded 15 mg (7%) of sulfur, mp 118–120°, which gave no depression in melting point when mixed with an authentic sample. Naphthalene (292 mg, 29%), mp 79–80°, was eluted next. A mixture melting point with an authentic sample was not depressed and the nmr spectra of the two samples were identical.

2-Chloro-1-benzothiepin (27). Method A.—A solution of potassium *tert*-butoxide (3.55 g, 31.7 mmol) in tetrahydrofuran (35 ml) was added dropwise over a 40-min period to a stirred solution of 2,2-dichloro-2,3-dihydro-1-benzothiepin (6.9 g, 30 mmol) in tetrahydrofuran (25 ml) at 3°. The mixture was allowed to come to room temperature and stirred vigorously for 4 hr. After the reaction mixture was concentrated (below 25°) under reduced pressure, H_2O (20 ml) was added and the aqueous solution was extracted with Skelly F. The extract was washed with H_2O and dried ($MgSO_4$) and the solution was chromatographed on alumina (A-540, 100 g) using Skelly F as the eluent. The initial yellow-colored fractions were combined and rapid removal of the solvent (below 15°) under reduced pressure gave 2.25 g (39%) of 2-chloro-1-benzothiepin (**27**) as a yellow oil: ir (CCl_4) 3070 (m), 3030 (m), 1920 (w), 1810 (w), 1710 (w), 1680 (w), 1610 (w), 1570 (m), 1470 (m), 1430 (m), 1300 (w), 1280 (w), 1260 (w), 1220 (w), 1180 (w), 1120 (w), 1060 (w), 1030 (w), 1000 (w), 960 (w), 910 (s), 860 (m), 820 (m), 710 cm^{-1} (m); nmr ($CDCl_3$) δ 7.34–7.18 (m, 4, aromatic H's), 7.01 (d, 1, J = 11.5 Hz, C_5 H), 6.45 (d, 1, J = 6 Hz, C_3 H), 6.18 (d d, 1, $J_{C_4-C_5}$ = 11.5, $J_{C_4-C_3}$ = 6 Hz, C_4 H); mass spectrum (70 eV) *m/e* (rel intensity) 196 (16), 194 (40), 164 (38), 162 (100), 159 (29), 128 (16), 127 (31), 126 (17), 115 (31), 105 (17).

Method B.—Redistilled thionyl chloride (2.4 g, 0.02 mol) in CH_2Cl_2 (10 ml) was added dropwise over 45 min to a refluxing solution of 2-chloro-5-hydroxy-4,5-dihydro-1-benzothiepin[5] (**29**, 3.0 g, 0.013 mol) and the reaction mixture was refluxed for 3 hr. After the CH_2Cl_2 was removed, mixed octanes (25 ml) were added and the solution was refluxed for 16 hr. The solvent was removed under reduced pressure and left a residue of 2.6 g (87%) of crude 2,5-dichloro-4,5-dihydro-1-benzothiepin (**30**); ir (neat) showed the absence of OH.

The sample of 2,5-dichloro-4,5-dihydro-1-benzothiepin prepared as described above from **29** (2.00 g, 0.0087 mol) and thionyl chloride (1.60 g, 0.013 mol) was dissolved in THF (10 ml) and to this solution was added dropwise a solution of potassium *tert*-butoxide (0.98 g, 0.0087 mol) in THF (10 ml). After the reaction mixture remained at room temperature for 6 hr, Skelly B (80 ml) was added and the mixture was filtered through Filter-Cel. The material insoluble in THF was dissolved in H_2O and acidified with nitric acid and upon treatment with silver nitrate gave an

81% yield of silver chloride. The Skelly B was removed from the above filtrate and the black residue was chromatographed on alumina (Alcoa F-20, 120 g), Elution with Skelly F gave 551 mg (33%) of 2-chloro-1-benzothiepin as a yellow oil. The infrared spectrum of this material was comparable with that of the sample from method A.

Pyrolysis of this sample produced α-chloronaphthalene (85%) and sulfur (19%); see the last experiment.

2-Chloro-1-benzothiepin 1,1-Dioxide (31). Method A.—Powdered potassium *tert*-butoxide (67 mg, 0.65 mmol) was added in one portion to a solution of 2,2-dichloro-2,3-dihydro-1-benzothiepin 1,1-dioxide (132 mg, 0.5 mmol) in tetrahydrofuran (10 ml), and, after the mixture was stirred at room temperature for 3 hr, it was poured into H_2O. The aqueous solution was extracted with $CHCl_3$, and the extract was washed with H_2O and dried ($MgSO_4$). The solvent was removed under reduced pressure and left 85 mg of a residue. Recrystallization of the solid from 95% ethanol gave 57 mg (58%) of 2-chloro-1-benzothiepin 1,1-dioxide: mp 139–140° (lit.[18] mp 139.5–140°); nmr ($CDCl_3$) δ 8.28–8.05 (m, 1, C_9 H), 7.86–7.70 (m, 3, C_6, C_7, C_8 H's), 7.56 (d, 1, J = 12 Hz, C_5 H), 7.10 (d, 1, J = 7.5 Hz, C_3 H), 6.70 (d d, 1, $J_{C_4-C_5}$ = 12, $J_{C_4-C_3}$ = 7.5 Hz, C_4 H); mass spectrum (70 eV) *m/e* (rel intensity) 228 (16), 226 (35), 181 (6), 164 (45), 162 (100), 127 (47), 126 (27), 115 (14). A mixture melting point with an authentic sample[18] of **31** was not depressed.

Method B.—A solution of 2-chloro-1-benzothiepin (584 mg, 3 mmol) in $CHCl_3$ (5 ml) was added dropwise to a stirred suspension of *m*-chloroperbenzoic acid (2.07 g, 12 mmol) in $CHCl_3$ (20 ml) maintained at −20°. The reaction mixture was allowed to come to room temperature and stirred for 10 hr, and the insoluble *m*-chlorobenzoic acid was filtered. The filtrate was washed with 10% $NaHCO_3$ solution and H_2O and dried ($MgSO_4$). After the solvent was removed under reduced pressure, the residue (780 mg) was chromatographed on alumina (A-540, 120 g). Elution with pentane gave 203 mg (42%) of α-chloronaphthalene, identified by its nmr spectrum, contaminated with some sulfur. Further elution with 20–100% of $CHCl_3$–pentane gave 112 mg (16%) of crude 2-chloro-1-benzothiepin 1,1-dioxide, mp 132–134°, which after recrystallization from 95% ethanol afforded 70 mg (10%) of pure **31**, mp 139–140° (lit.[18] mp 139.5–140°). A mixture melting point with an authentic sample was not depressed and the spectral properties of this sample were identical with those from method A.

4-Chloro-1-benzothiepin (28).—A solution of 2,4-dichloro-2,3-dihydro-1-benzothiepin[1a] (500 mg, 2.16 mmol) in *tert*-butyl alcohol (14 ml) was added in one portion to a solution of potassium *tert*-butoxide (246 mg, 2.20 mmol) in *tert*-butyl alcohol (24 ml). After the reaction mixture was stirred for 50 min, the turbid orange solution was poured into H_2O (150 ml), the aqueous solution was extracted with $CHCl_3$, and the extract was washed with H_2O and dried ($MgSO_4$). The solvent was removed under vacuum and gave 330 mg (79%) of 4-chloro-1-benzothiepin (**28**) as a yellow oil: ir ($CHCl_3$) 3070 (w), 3005 (w), 1610 (s), 1470 (s), 1370 (m), 1125 (m), 1005 (s), 945 (w), 890 (s), 855 (m), 840 cm^{-1} (m); nmr ($CDCl_3$) δ 7.5–6.8 (m, 5, aromatic H's and C_5 H), 6.15 (d, 1, $J_{C_3-C_2}$ = 9 Hz, C_3 H), 5.78 (d, 1, $J_{C_2-C_3}$ = 9 Hz, C_2 H); mass spectrum (70 eV) *m/e* (rel intensity) 196 (13), 194 (39), 164 (52), 162 (100), 159 (39), 127 (61), 126 (35), 115 (45), 105 (44). 4-Chloro-1-benzothiepin can be further purified by chromatography on alumina with elution with Skelly F.

When a solution of 2,4-chloro-2,3-dihydro-1-benzothiepin (360 mg, 1.56 mmol) and potassium *tert*-butoxide (180 mg, 1.60 mmol) in *tert*-butyl alcohol (12 ml) was heated at 70° for 90 min and processed as above, chromatography on Alcoa F-20 (20 g) with elution by Skelly F provided 105 mg (40%) of β-chloronaphthalene, mp 56–57°. A mixture melting point with an authentic sample was not depressed.

A reaction of 2,4-dichloro-2,3-dihydro-1-benzothiepin and LiCl in DMF at 65° for 60 min also resulted in the formation of β-chloronaphthalene (22% yield).

4-Chloro-1-benzothiepin 1,1-Dioxide (32). Method A.—The reaction mixture of 2,4-dichloro-2,3-dihydro-1-benzothiepin 1,1-dioxide[1a] (1.00 g, 4.41 mmol) and potassium *tert*-butoxide (0.49 g, 4.41 mmol) in DMSO (30 ml) was stirred for 15 min and processed as described in the preparation of 1-benzothiepin 1,1-dioxide (method A) and gave 0.40 g (40%) of crude 2,4-dichloro-2,3-dihydro-1-benzothiepin 1,1-dioxide, mp 174–183°, and 0.17 g (17%) of crude 4-chloro-1-benzothiepin 1,1-dioxide (**32**), mp 139.5–143°. Chromatography of 0.072 g of the latter product on alumina (A-540, 40 g) gave a mixture which was recrystallized from absolute ethanol to give 0.03 g (7% corrected from total crude yield) of pure **32**: mp 154–155°; ir ($CHCl_3$) 1320 and 1150 cm^{-1} (–SO_2–); nmr ($CDCl_3$) δ 8.41–8.10 (m, 1, C_9 H), 7.90–7.62 (m, 3, C_6, C_7, C_8 H's and C_5 H), 6.97 [d, 2 (total weight of C_2 H and C_3 H), $J_{C_3-C_2}$ = 14 Hz, C_3 H], 6.94 [d, 2 (total weight of C_3 H and C_2 H), $J_{C_2-C_3}$ = 14 Hz, C_2 H]; mass spectrum (70 eV) *m/e* (rel intensity) 228 (6), 226 (22), 164 (37), 162 (100), 127 (38).

Anal. Calcd for $C_{10}H_7ClO_2S$: C, 52.98; H, 3.11; Cl, 15.64. Found: C, 52.58; H, 3.00; Cl, 15.70.

Method B.—A solution of 4-chloro-1-benzothiepin (281 mg, 1.45 mmol) in $CHCl_3$ (3 ml) was added in one portion to a stirred suspension of *m*-chloroperbenzoic acid (560 mg, 3.26 mmol) in $CHCl_3$ (7 ml) at −18°. The reaction mixture was stirred at 10° for 21 hr and filtered, and the $CHCl_3$ filtrate was washed with Na_2CO_3 and H_2O and dried ($MgSO_4$). After the solvent was removed under vacuum, the residue (174 mg) was treated with Skelly F (2 × 3 ml) and gave 91 mg (40%) of 4-chloro-1-benzothiepin 1,1-dioxide (**32**), mp 145–155°. Recrystallization of the crude solid from 95% ethanol–benzene gave pure **32**, mp 155–157° dec. The ir spectrum of this sample was identical with that of **32** from method A.

Concentration of the Skelly F washings afforded 63 mg (27%) of β-chloronaphthalene identified by comparison of its ir spectrum with that of an authentic sample.

Thermal Decomposition of the 1-Benzothiepins. Method A.—Approximately 1 *M* solutions of 1-benzothiepin, 2-chloro-1-benzothiepin, and 4-chloro-1-benzothiepin in CCl_4 were prepared and the decomposition to sulfur and the corresponding naphthalenes was monitored by nmr spectroscopy at room temperature. The disappearance with time of the 1-benzothiepins is recorded in Table III.

TABLE III

THERMAL DECOMPOSITION OF 1-BENZOTHIEPINS[a]

	Benzothiepin remaining, %		
Time, days	1-Benzothiepin	2-Chloro-1-benzothiepin	4-Chloro-1-benzothiepin
4.5 hr	80	91	80
1	35	67	
2	12	47	22
3	3	33	15
4	0	25	5
5		16	0
9		7	
11		0	

[a] See Thermal Decomposition of 1-Benzothiepin, Method A. When 2-chloro-1-benzothiepin was stored in the cold, very little decomposition occurred over a 3-month period.

After the decomposition of 1-benzothiepin (113 mg, 0.59 mmol) was complete, the solvent was evaporated and the resulting solid was triturated with pentane (2 × 10 ml). The pentane was evaporated and left 0.069 g (78%) of naphthalene, mp 63–65°. The nmr spectrum was identical with that of an authentic sample.

A similar work-up from the decomposition of 2-chloro-1-benzothiepin (0.113 g, 0.59 mmol) gave 0.05 g (68%) of sulfur, mp 118–119°, mmp with authentic sample 118–119°, which precipitated from the residue after removal of CCl_4. The pentane solution of the residual oil was dried and upon removal of the solvent gave 0.103 g (93%) of α-chloronaphthalene; ir and nmr spectra were identical with those of an authentic sample.

Method B.—2-Chloro-1-benzothiepin (551 mg, 2.83 mmol) was heated neat in a free flame for a few seconds and the pyrolysate was chromatographed on alumina (Alcoa F-20, 60 g). Elution with pentane gave 17 mg (19%) of sulfur, mp 120–121°, mmp with an authentic sample 120–121°, and 389 mg (85%) of α-chloronaphthalene, ir spectrum identical with that of an authentic sample.

A solution of 4-chloro-1-benzothiepin (172 mg, 0.89 mmol) in benzene (15 ml) was refluxed for 30 min, the solvent was removed under vacuum, and the residue (160 mg) was chromatographed on alumina (Alcoa F-20, 20 g). Elution with Skelly F gave 137 mg of β-chloronaphthalene, mp 56–57°. A mixture melting point with an authentic sample was not depressed and the ir spectrum was identical with that of an authentic sample.

(18) V. J. Traynelis and D. M. Borgnaes, *J. Org. Chem.*, **37**, 3824 (1972).

Registry No.—7, 21609-62-1; 8, 41887-72-3; 9, 264-82-4; 10, 41887-74-5; 11, 41887-75-6; 12, 41887-76-7; 13, 41887-77-8; 14, 41887-78-9; 15, 41887-79-0; 16, 41887-80-3; 17, 41887-81-4; 18, 41887-82-5; 19, 41887-83-6; 20, 41887-84-7; 21, 41887-85-8; 25, 41887-86-9; 27, 41887-87-0; 28, 41887-88-1; 29, 41887-89-2; 30, 41887-90-5; 31, 36287-21-5; 32, 41887-92-7.

Seven-Membered Heterocycles. VIII. 1-Benzothiepin Sulfoxides and a Convenient Synthesis of Sulfoxides[1,2]

VINCENT J. TRAYNELIS,* Y. YOSHIKAWA,[3] AND STANLEY M. TARKA

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

JOEL R. LIVINGSTON, JR.[4]

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

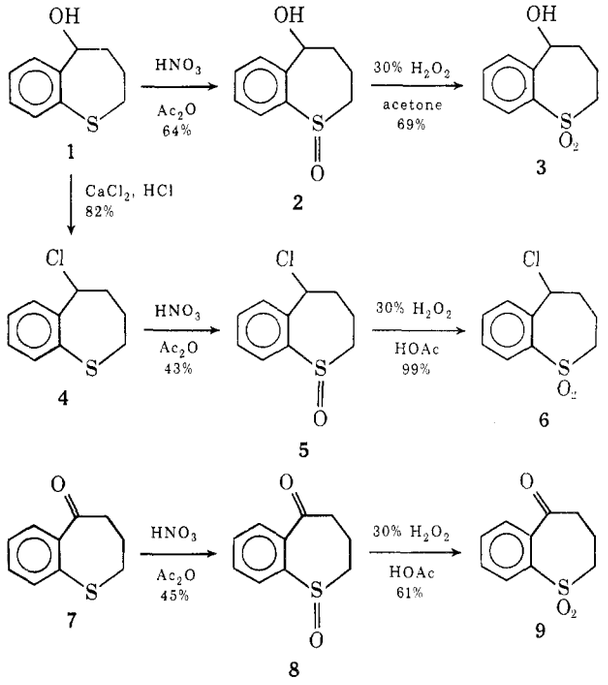
Received June 15, 1973

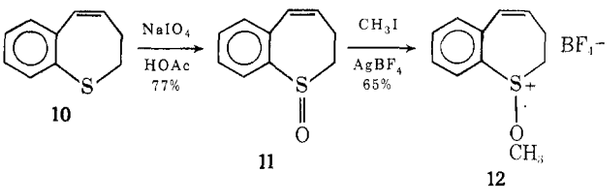
The following sulfoxides were prepared by the oxidation of the corresponding sulfides with a nitric acid–acetic anhydride mixture: 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**2**, 64% yield), 5-chloro-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**5**, 43% yield), and 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1-oxide (**8**, 45% yield). 2,3-Dihydro-1-benzothiepin 1-oxide (**11**) was available by oxidation of the sulfide **10** with sodium metaperiodate or sulfuryl chloride (−78°) followed by hydrolysis. The latter method has been shown to be a general procedure for the synthesis of sulfoxides in high yields. The intermediate in this synthesis appears to be a chlorine sulfide complex which at low temperature is best represented by the tetracovalent sulfur structure **14b**.

In the course of our synthetic studies in the 1-benzothiepin system[1,5–8] we became interested in 1-benzothiepin sulfoxides as potentially useful synthetic intermediates, particularly 2,3-dihydro-1-benzothiepin 1-oxide (**11**). We now wish to report the synthetic methods used to produce these sulfoxides and the development of a new technique which appears to be a general and simple sulfoxide synthesis.

1-Benzothiepin Sulfoxides.—The initial sulfoxides prepared were 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**2**) and 5-chloro-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**5**). The reaction entailed oxidation of sulfides **1** and **4** with fuming nitric acid and acetic anhydride as initially reported by Pollard and Robinson[9] and further developed by Bordwell and Boutan.[10] The yields of products were moderate and the structural assignments were based on elemental analyses, spectral data, and the conversion of the sulfoxides to the corresponding sulfones **3** and **6**. A similar reaction sequence was performed in the conversion of ketone **7** to 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1-oxide (**8**) and subsequent oxidation to sulfone **9**.

Attempts to dehydrate alcohol sulfoxide **2** or to dehydrochlorinate sulfoxide **5** were all unsuccessful in leading to 2,3-dihydro-1-benzothiepin 1-oxide (**11**). Synthesis of **11** was initially achieved by sodium metaperiodate oxidation[11] of 2,3-dihydro-1-benzothiepin (**10**). Sulfoxide **11** was an oil with ir and nmr spectra consistent with the assigned structure and was further characterized by conversion to 1-methoxy-2,3-dihydro-1-benzothiepinium tetrafluoroborate (**12**).





Convenient Synthesis of Sulfoxides.—A new method for the synthesis of sulfoxides emerged from a study of the chlorination of ketone **7**[7] and 2,3-dihydro-1-benzothiepin (**10**)[1] with sulfuryl chloride. The reaction of sulfides with sulfuryl chloride readily produces α-chloro

(1) For part VII in this series see V. J. Traynelis, Y. Yoshikawa, J. C. Sih, L. J. Miller, and J. R. Livingston, Jr., *J. Org. Chem.*, **38**, 3978 (1973).

(2) (a) Presented in part at the 4th Central Regional Meeting of the American Chemical Society, Pittsburgh, Pa., May 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.

(3) Abstracted from a portion of the Ph.D. Dissertation submitted by Y. Y. in May 1973 at West Virginia University.

(4) Abstracted from a portion of the Ph.D. Dissertation submitted by J. R. L., Jr., in March 1962 at the University of Notre Dame.

(5) V. J. Traynelis and J. R. Livingston, Jr., *J. Org. Chem.*, **29**, 1092 (1964).

(6) V. J. Traynelis and D. M. Borgnaes, *J. Org. Chem.*, **37**, 3824 (1972).

(7) V. J. Traynelis, J. C. Sih, Y. Yoshikawa, R. F. Love, and D. M. Borgnaes, *J. Org. Chem.*, **38**, 2623 (1973).

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

(9) A. Pollard and R. Robinson, *J. Chem. Soc.*, 3090 (1926).

(10) F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, **79**, 717 (1957).

(11) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).