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]

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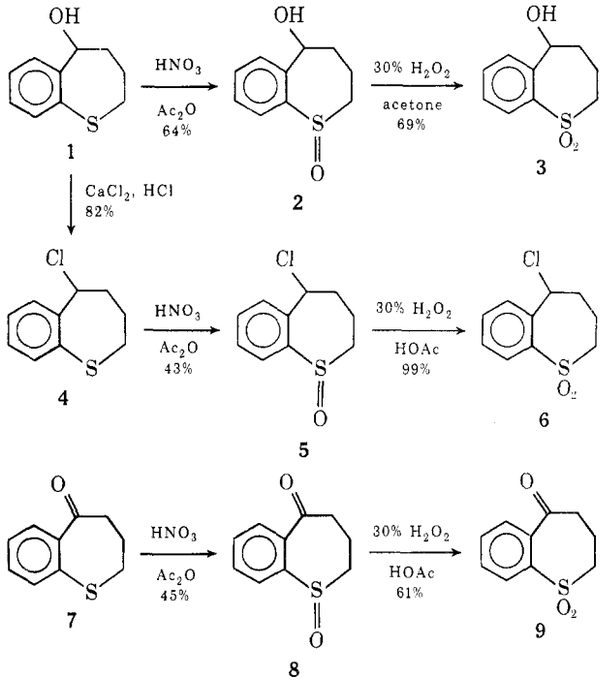
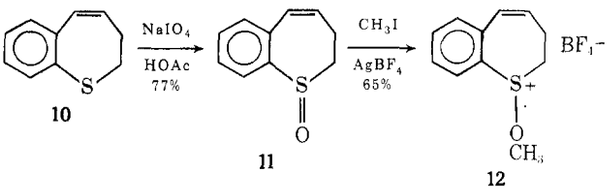
The following sulfoxides were prepared by the oxidation of the corresponding sulfides with a nitric acid–acetic anhydride mixture: 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**2**, 64% yield), 5-chloro-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**5**, 43% yield), and 3,4-dihydro-1-benzothiepin-5(2*H*)-one 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).

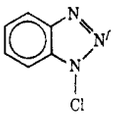
(8) V. J. Traynelis, J. C. Sih, and D. M. Borgnaes, *J. Org. Chem.*, **38**, 2629 (1973).

(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).

TABLE I
OXIDATION OF SULFIDES TO SULFOXIDES

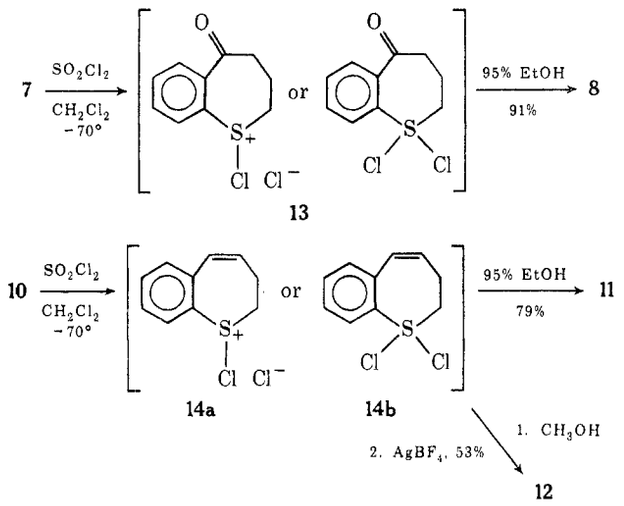
Sulfoxide	Yield, %						
	SO_2Cl_2	$NaIO_4$[a]	t-BuOCl[b]	$PhICl_2$[c]	DABCO $2Br_2$[d]	NBS[e]	
2,3-Dihydro-1-benzothiepin 1-oxide (11)	79	77[g]					
3,4-Dihydro-1-benzothiepin-5(2*H*)-one 1-oxide (8)	91						
Phenyl sulfoxide	95	98	94	96	95	93	
Phenyl methyl sulfoxide	97	99	90	86	85[h]	0[i]	92
Benzyl sulfoxide	99	96	64	98	70[j]	86	
n-Octadecyl ethyl sulfide	90			85[k]		76[k]	87[l]
Tetramethylene sulfoxide	60						70

[a] See ref 11. [b] L. Skattebøl, B. Boulette, and S. Solomon, *J. Org. Chem.*, **32**, 3111 (1967). [c] G. Barbier, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc.*, 659 (1968). [d] Bromine complex of 1,4-diazabicyclo[2.2.2]octane: S. Oae, Y. Onishi, S. Kozuka, and N. Tagaki, *Bull. Chem. Soc. Jap.*, **39**, 364 (1966). [e] *N*-Bromosuccinimide: R. Harville and S. F. Reed, Jr., *J. Org. Chem.*, **33**, 3976 (1968). [f] W. D. Kingsbury and C. R. Johnson, *Chem. Commun.*, 365 (1969). [g] This work. [h] The yield represents that of *p*-tolyl methyl sulfoxide. [i] W. Tagaki, K. Kikukawa, K. Ando, and S. Oae, *Chem. Ind. (London)*, 1624 (1969). [j] The yield represents that of ethyl benzyl sulfoxide. [k] This yield represents that of *n*-propyl sulfoxide. [l] This yield represents that of isopropyl sulfoxide.

sulfides[12] and has been proposed to proceed by a polar mechanism involving chlorosulfonium salts as initial intermediates.[12a,13] These chlorine sulfide salts or complexes are more commonly generated by the direct reaction of chlorine with sulfides.[14-19] In addition to the ease with which these complexes decompose to α-chloro sulfides, the complexes can also be hydrolyzed to sulfoxides.[14]

Thus the reaction of sulfuryl chloride and sulfides at low temperatures (−40 to −70°) led to chlorine sulfide complexes which were stable at these temperatures, and low-temperature hydrolysis with 95% ethanol converted the complexes to the corresponding sulfoxides. This technique was first applied with 3,4-dihydro-1-benzothiepin-5(2*H*)-one (**7**) to acquire evidence for the intermediate chlorine sulfide complex **13** which was hydrolyzed to sulfoxide **8** in 91% yield. Secondly, the reaction of 2,3-dihydro-1-benzothiepin and sulfuryl chloride, which gave *cis*- and *trans*-4,5-dichloro-2,3,4,5-tetrahydro-1-benzothiepin,[1] was shown to proceed through the chlorine sulfide intermediate **14** by diverting **14** *via* hydrolysis to sulfoxide **11** in 79% yield. In addition further support for intermediate **14** arose from treatment with anhydrous methanol followed by silver tetrafluoroborate to form the methoxysulfonium salt **12**.

These reactions of the chlorine sulfide complexes appeared to have general potential in the synthesis of sulfoxides and methoxysulfonium salts. A series of sulfides including diaryl, aryl alkyl, alkyl, and heterocyclic were subjected to the low-temperature reaction with sulfuryl chloride followed by hydrolysis and were converted to sulfoxides in excellent yields. Table I summarizes these results and compares this method of sulfoxide synthesis to others in the literature.[20,21] The sulfuryl chloride, hydrolysis sequence is effective in the synthesis of sulfoxides in the presence of certain functional groups (carbonyl and olefinic groups were the only ones examined), avoids overoxidation to sulfones, utilizes mild conditions (−78°), employs inexpensive materials, and does not appear to be limited to certain types of sulfides.



The nature of the chlorine sulfide complex in these reactions raises the question of a chlorosulfonium chloride or a tetracovalent dichlorosulfur structure. Lawson and Dawson[14] reported a crystalline chlorine sulfide complex of β,β′-dichloroethyl sulfide isolated below 0° and Meerwein and coworkers[16] prepared dimethylchlorosulfonium salts (hexachloroantimonate, tetrafluoroborate, etc.). In both cases the structures were represented as salt-like. The intermediate proposed in the reaction (at 0° or higher) of sulfuryl chloride and sulfides to form α-chloro sulfides was a chlorosulfonium chloride.[12a,13] However, recent reports in

(12) (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).
(13) D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969).
(14) W. E. Lawson and T. P. Dawson, *J. Amer. Chem. Soc.*, **49**, 3119 (1927).
(15) H. Bohme and H. Grand, *Justus Liebigs Ann. Chem.*, **577**, 68 (1952).
(16) H. Meerwein, K. Zenner, and R. Gipp, *Justus Liebigs Ann. Chem.*, **688**, 67 (1965).
(17) R. J. Maner, Ph.D. Dissertation, University of Iowa, 1968.
(18) H. Kwart and H. Omura, *J. Amer. Chem. Soc.*, **93**, 7250 (1971), and references cited therein.
(19) (a) E. J. Corey and C. U. Kim, *J. Amer. Chem. Soc.*, **94**, 7586 (1972); (b) E. J. Corey, C. U. Kim, and M. Takeda, *Tetrahedron Lett.*, 4339 (1972).
(20) C. R. Johnson and J. C. Sharp, *Quart. Rep. Sulfur Chem.*, **4**, 1 (1969).
(21) F. Montanari and M. Cinquini, *Mech. React. Sulfur Compounds*, **3**, 121 (1968).

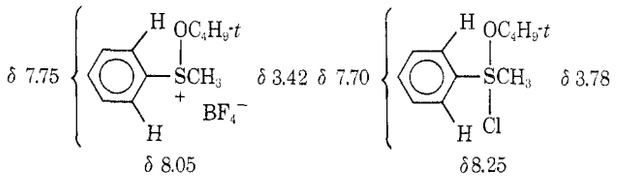
TABLE II

LOW-TEMPERATURE NMR DATA FOR 2,3-DIHYDRO-1-BENZOTHIEPIN (10), 1-METHOXY-2,3-DIHYDRO-1-BENZOTHIEPINIUM TETRAFLUOROBORATE (12), AND 2,3-DIHYDRO-1-BENZOTHIEPIN CHLORINE COMPLEX 14 AT −50°

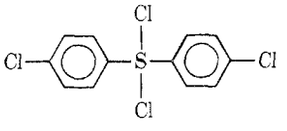
	δ		
	10	12	14
C_2 H, C_3 H	2.84 (broad s)	3.6-4.6 (br m)	4.75 (t, J = 5.5 Hz)
		3.0 (br s)	3.13 (d t, J = 5.5 Hz)
C_4 H	5.92 (d t, J = 13 and 3.5 Hz)	6.01 (br d, J = 12 Hz)	6.27 (d t, J = 5.5 and 11 Hz)
C_5 H	6.45 (d, J = 13 Hz)	6.32 (d, J = 12 Hz)	6.57 (J = 11 Hz)
C_6, C_7, C_8 H's	7.10 (m)	7.43 (m)	7.40 (m)
C_9 H	7.34 (m)	7.87 (m)	8.04 (m)
OCH_3		3.98 (s)	

the literature[22-25] describe tetracovalent sulfur species which in some cases have been isolated[22] and confirmed by X-ray crystallography[22,23] and in other cases have been detected as reaction intermediates by spectral studies[24] and the nature of the reaction products.[25]

In the oxidation of thioanisole with *tert*-butyl hypochlorite, Johnson and Rigau[24] proposed the intermediacy of a tetracovalent sulfur species **16** on the basis of a low-temperature nmr study. The two ortho hydrogens and methyl hydrogens in **16** appeared significantly at lower field in contrast to analogous hydrogens in the trivalent salt **15**. Similar downfield shifts in the nmr were reported[17] for the ortho hydrogens of bis(*p*-chlorophenyl) sulfide chlorine complex **17** when compared to



15 **16**



17

the corresponding hydrogen position for the sulfide. The tetracovalent sulfur structure of the complex **17** was supported by an X-ray study.[23]

We have examined the low-temperature (−50°) nmr spectrum of the intermediate **14** from the reaction of sulfuryl chloride with 2,3-dihydro-1-benzothiepin (**10**) and compared this spectrum with those of **10** and 1-methoxy-2,3-dihydro-1-benzothiepinium tetrafluoroborate (**12**) at −50°. The results appear in Table II and the downfield shift of the C_9-H and C_2-H resonances in **14** compared with the corresponding hydrogens in the methoxysulfonium salt **12** and the sulfide **10** parallel the results reported by Johnson and Rigau.[24] In view of the magnitude of the C_9-H and particularly the C_2-H shifts in **14** compared with **13**, we favor the assignment of the dichlorosulfurane structure **14b** for the reaction intermediate at −50° in preference to the chlorosulfonium structure **14a**. Similar deshielding affects on the C_9 hydrogen, resulting from geometric and electronic change on sulfur, can be observed by increasing the number of oxygen atoms on sulfur in going from 2,3-dihydro-1-benzothiepin (**10**) [C_9 H, δ 7.40 (m)] to 2,3-dihydro-1-benzothiepin 1-oxide (**11**) [C_9 H, δ 7.88 (m)] and 2,3-dihydro-1-benzothiepin 1,1-dioxide [C_9 H, δ 8.10 (m)]. Also consistent with structure **14b** is the multiplicity of the C_2 hydrogens (equivalent hydrogens give rise to a triplet) in contrast to **13** where the nonequivalent C_2 hydrogens appear as a complex multiplet.

In conclusion the low-temperature reaction of sulfuryl chloride and sulfides forms a chlorine sulfide complex which is readily hydrolyzed to the corresponding sulfoxide in high yield. These intermediates should also find application in the new transformations recently described by Corey and coworkers.[19]

Experimental Section[26]

General Oxidative Procedure with Sulfuryl Chloride.—A solution of sulfuryl chloride in CH_2Cl_2 was added dropwise with stirring to an equimolar amount of the sulfide in CH_2Cl_2 solution maintained at −70°. After the reaction mixture was stirred for 15–30 min and kept at low temperature, −40 to −78° for 2–24 hr, 95% ethanol was added slowly and the solution was allowed to come to room temperature. The reaction mixture was neutralized with $NaHCO_3$, Na_2CO_3, or K_2CO_3, the organic layer was separated, washed (H_2O), and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue which remained was distilled, recrystallized, or characterized without further treatment and shown to be the corresponding sulfoxides.

2,3-Dihydro-1-benzothiepin 1-Oxide (11). Method A.[27]—A solution of sodium metaperiodate (104 ml of 0.50 *M*, 0.052 mol) was added to 2,3-dihydro-1-benzothiepin[28] (7.00 g, 0.043 mol) in glacial acetic acid (110 ml) and the reaction mixture was stirred for 31 hr at ice-bath temperature. The solid was filtered and the aqueous solution was extracted with $CHCl_3$. After the extract was washed with 15% $NaHCO_3$ solution and H_2O and dried ($MgSO_4$), the solvent was removed under vacuum and gave 5.84 g (77%) of 2,3-dihydro-1-benzothiepin 1-oxide (**11**) as a yellow oil: ir (neat) 3000 (m), 1645 (m), 1470 (m), 1415 (m), 1070, 1030 (s, >S=O), 750 cm^{-1} (s); nmr ($CDCl_3$) δ 8.00–7.76 (m, 1, C_9-H), 7.60–7.10 (m, 3, C_6, C_7, C_8 H's), 6.52 (d, 1, $J_{C_5-C_4}$ = 12.5 Hz, C_5-H), 5.97 (d t, 1, $J_{C_4-C_3}$ = 5, $J_{C_4-C_5}$ = 12.5 Hz, C_4 H), 3.40 (t, 2, $J_{C_2-C_3}$ = 7.0 Hz, $-SOCH_2CH_2$), 2.64 (d t, 2, $J_{C_3-C_2}$ = 7.0, $J_{C_3-C_4}$ = 5 Hz, $-SOCH_2CH_2-$).

Method B.—The above general oxidative procedure was used with 2,3-dihydro-1-benzothiepin[11] (2.0 g, 12 mmol) in CH_2Cl_2 (15 ml) at −70° and sulfuryl chloride (1 ml, 12 mmol) in CH_2Cl_2 (3 ml) with a reaction time of 3 hr at −70°. Addition of 95% ethanol (10 ml) and work-up as above gave 1.73 (79%) of 2,3-

(22) R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 4997, 5003 (1972); I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, **94**, 5010 (1972), and related papers.

(23) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969).

(24) C. R. Johnson and J. J. Rigau, *J. Amer. Chem. Soc.*, **91**, 5398 (1969).

(25) T. Durst and K. C. Tin, *Can. J. Chem.*, **49**, 2374 (1971).

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

(27) This procedure is taken from the Ph.D. Dissertation of J. C. Sih, West Virginia University, Dec 1971.

(28) V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *J. Org. Chem.*, **27**, 2377 (1962).

dihydro-1-benzothiepin 1-oxide as a yellow oil, ir and nmr spectra identical with those of the above sample.

1-Methoxy-2,3-dihydro-1-benzothiepinium Tetrafluoroborate (12). Method A.—Silver tetrafluoroborate (1.2 g, 5.8 mmol) and methyl iodide (1.24 g, 11.6 mmol) in CH_2Cl_2 (5 ml) were added to a stirred solution of 2,3-dihydro-1-benzothiepin 1-oxide (**11**, 1.0 g, 5.8 mmol) in CH_2Cl_2 (15 ml) and the mixture was stirred at room temperature for 3.5 hr. After the reaction mixture was filtered, ether was added to the filtrate until the cloud point and the oil, which separated, crystallized slowly to give 1.0 g (65%) of 1-methoxy-2,3-dihydro-1-benzothiepinium tetrafluoroborate (**12**): mp 106–108°; ir (KBr) 3025 (w), 1470 (m), 1060 (br, s), 775 cm^{-1} (s); nmr ($CDCl_3$) δ 8.20–8.00 (m, 1, C_9 H), 7.84–7.48 (m, 3, C_6, C_7, C_8 H's), 6.64 (d, 1, $J_{C_5-C_4}$ = 12 Hz, C_5 H), 6.23 (d t, 1, $J_{C_4-C_5}$ = 12, $J_{C_4-C_3}$ = 5 Hz, C_4 H), 4.80–3.67, sharp peak 4.07 (m, 5, C_2 H's and $-OCH_3$, 4.07 peak), 3.24–2.87 (m, 2, C_3 H's).

Anal. Calcd for $C_{11}H_{13}BF_4OS$: C, 47.17; H, 4.68. Found: C, 47.08; H, 4.49.

Method B.—After a solution of 2,3-dihydro-1-benzothiepin[28] (0.81 g, 5.0 mmol) and sulfuryl chloride (0.71 g, 5.3 mmol) in CH_2Cl_2 (5 ml) was kept at −78° for 2 days, methanol (0.2 ml) in CH_2Cl_2 (2 ml) at −78° was added to the reaction mixture and the solution was allowed to come to room temperature (about 90 min). The reaction mixture was again cooled to −50°, silver tetrafluoroborate (2.0 g, 10 mmol) was added, and the mixture was maintained at −78° overnight and then stirred at 5–8° for 5 hr. After the precipitate was filtered and washed with CH_2Cl_2, the solvent was removed under reduced pressure from the combined filtrate and washings and left 1.69 g of an oily residue. The oil solidified and was recrystallized from CH_2Cl_2–ether to give 0.744 g (53%) of 1-methoxy-2,3-dihydro-1-benzothiepinium tetrafluoroborate (**12**), mp 106–107°. A mixture melting point with the sample from method A was not depressed and their nmr spectra were identical.

3,4-Dihydro-1-benzothiepin-5(2*H*)-one 1-Oxide (8). Method A.—An oxidizing mixture was prepared by dropwise addition of red fuming nitric acid (*d* 1.52, 40 ml) to acetic anhydride (20 ml) cooled in an ice bath. This cold solution was added dropwise with stirring over a period of 20 min to a solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one[29] (10.0 g, 0.056 mmol) in acetic anhydride (40 ml) at ice-bath temperature and the reaction mixture was placed in a refrigerator for 20 hr. After the mixture was poured onto crushed ice (100 g) and neutralized by addition of 20% NaOH solution with vigorous stirring while the temperature was maintained below 30°, sodium bisulfite (5 g) was added and the solution was extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and the $CHCl_3$ was removed under reduced pressure. The residual oil was dried in a vacuum desiccator overnight and extracted with boiling cyclohexane, which, after treatment with Norit, gave 4.85 g (45%) of 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1-oxide (**8**) as white, crystalline needles: mp 70.5–72.5°; ir ($CHCl_3$) 1665 (>C=O), 1050 cm^{-1} (br, >S=O); nmr ($CDCl_3$) δ 8.10–7.35 (m, 4, aromatic H's), 3.76–2.80 (m, 4, $-SOCH_2CH_2-CH_2CO-$), 2.63–1.94 (m, 2, $-SOCH_2CH_2CH_2CO-$). An analytical sample, mp 72.5–73.5°, was prepared by recrystallization from cyclohexane.

Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19. Found: C, 61.53; H, 5.11.

A 2,4-dinitrophenylhydrazone, mp 176.5° after recrystallization from ethanol, was prepared in the usual way.

Anal. Calcd for $C_{16}H_{14}N_4O_5S$: C, 51.32; H, 3.78. Found: C, 51.37; H, 4.02.

Method B.—The procedure for preparation of **11**, method B, was used to convert 3,4-dihydro-1-benzothiepin-5(2*H*)-one[29] (2.0 g, 11.1 mmol) with sulfuryl chloride (1.55 g, 11.5 mmol) in CH_2Cl_2 (12 ml) followed by hydrolysis with 95% ethanol (15 ml) to 1.60 g (74%), recrystallized from cyclohexane, of 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1-oxide, mp 74–75°, ir and nmr identical with those spectra of the above sample.

3,4-Dihydro-1-benzothiepin-5(2*H*)-one 1,1-Dioxide (9).—A solution of 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1-oxide (**8**, 0.75 g, 0.004 mol), acetic acid (4 ml), and 30% H_2O_2 (2.5 ml) was allowed to stand overnight at room temperature and poured into H_2O and the precipitate was filtered. The solid was recrystallized from ethanol and gave 0.51 g (61%) of 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1,1-dioxide (**9**), mp 153–156° (lit.[29] mp 155–156°). A mixture melting point with an authentic sample was not depressed and the ir spectrum was identical with that of an authentic sample.

5-Hydroxy-2,3,4,5-tetrahydro-1-benzothiepin 1-Oxide (2).—The procedure described under 3,4-dihydro-1-benzothiepin-5(2*H*)-one 1-oxide (**8**), method A, was employed for the reaction of red fuming nitric acid (*d* 1.52, 2 ml) in acetic anhydride (12.5 ml) and 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin[29] (5.0 g, 0.028 mol) in acetic anhydride (35 ml) for 24 hr at refrigerator temperature. After work-up, the $CHCl_3$ extract, dried (Na_2SO_4), was treated with Skelly F and upon cooling in a deep freeze for 2 days gave 3.48 g (64%) of 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**2**): mp 103–106°; ir ($CHCl_3$) 3350 (OH), 1010 cm^{-1} (>S=O); nmr ($CDCl_3$) δ 7.87–7.54 (m, 1, C_9 H), 7.49–7.28 (m, 3, C_6, C_7, C_8 H's), 5.10 (br d, 1, C_5 H), 4.24 (br s, 1, OH), 3.12–1.66 (m, 6, $-SOCH_2CH_2CH_2CHOH-$). An analytical sample, mp 110–113°, was prepared by repeated recrystallization from benzene.

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.13; H, 6.16. Found: C, 61.25; H, 6.12.

5-Hydroxy-2,3,4,5-tetrahydro-1-benzothiepin 1,1-Dioxide (3). A solution of 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**2**, 0.4 g, 0.002 mol), acetone (2 ml), and 30% H_2O_2 (1.75 ml) was allowed to stand overnight, then refluxed for 30 min. The solvent was removed under reduced pressure and the residue was recrystallized from benzene to give 0.30 g (69%) of 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide, mp 128–129°. A second recrystallization of **3** from benzene raised the melting point to 136–139° (lit.[29] mp 141–142°). A mixture melting point with an authentic sample was not depressed and the ir spectrum was identical with that of an authentic sample.

5-Chloro-2,3,4,5-tetrahydro-1-benzothiepin (4).—Solid 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin[29] (9.0 g, 0.05 mol) was added in one portion to a vigorously stirred solution of $CaCl_2$ (25 g) in concentrated HCl (100 ml) and the mixture was heated on a steam bath for 30 min. The reaction mixture was poured onto ice (200 g) and extracted with ether and the extract was dried (Na_2SO_4). After the solvent was removed, distillation of the residue gave 8.06 g (82%) of 5-chloro-2,3,4,5-tetrahydro-1-benzothiepin (**4**): bp 79–81° (0.05–0.08 Torr) [lit.[30] bp 105–110° (0.4 Torr)]; $n^{20}D$ 1.6159; ir (neat) 2900 (s), 1450 (s), 1285 (m), 1238 (m), 1035 (m), 910 (m), 876 (m), 820 (m), 760 (s), 741 (s), 718 cm^{-1} (s); nmr ($CDCl_3$) δ 7.64–7.00 (m, 4, aromatic H's), 5.59 (d d, 1, J = 8.5 and 3.0 Hz, C_5 H), 2.72–2.54 (m, 2, $-SCH_2-CH_2-$), 2.48–1.66 (m, 4, $-SCH_2CH_2CH_2-$).

5-Chloro-2,3,4,5-tetrahydro-1-benzothiepin 1-Oxide (5).—A solution of 5-chloro-2,3,4,5-tetrahydro-1-benzothiepin (**4**, 5.0 g, 0.25 mol) in acetic anhydride (25 ml) was added to a solution of 70% nitric acid (40 ml) and acetic anhydride (25 ml) prepared as described above and maintained at 0°. After the mixture remained in the refrigerator for 10 hr and was poured onto ice, the solution was neutralized with 20% NaOH solution and the solid was collected and dried. Recrystallization of the crude material from benzene–Skelly B gave 2.02 g (43%) of white needles of 5-chloro-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**5**): mp 141–142°; ir ($CHCl_3$) 2980 (m), 1450 (m), 1068 (s), 1030 cm^{-1} (s, >S=O).

Anal. Calcd for $C_{10}H_{11}ClOS$: C, 55.94; H, 5.17. Found: C, 55.84; H, 5.13.

5-Chloro-2,3,4,5-tetrahydro-1-benzothiepin 1,1-Dioxide (6).—A solution of 5-chloro-2,3,4,5-tetrahydro-1-benzothiepin 1-oxide (**5**, 0.50 g, 0.0023 mol), 30% H_2O_2 (2 ml), and acetic acid (10 ml) was allowed to stand for 12 hr at room temperature and then heated on a steam bath for 30 min. The mixture was poured into H_2O (30 ml) and cooled (5° for 24 hr) and the product was filtered. Recrystallization of the solid from cyclohexane gave 0.53 g (99%) of 5-chloro-2,3,4,5-tetrahydro-1-benzothiepin 1,1-dioxide (**6**): mp 97–98.2°; ir ($CHCl_3$) 1300 (br), 1155, and 1120 cm^{-1} (>SO_2); nmr ($CDCl_3$) δ 8.20–7.93 (m, 2, C_9 H and C_6 H), 7.62–7.30 (m, 2, C_7, C_8 H's), 5.97 (d d, 1, J = 9 and 2 Hz), 3.36–3.00 (m, 2, $-SO_2CH_2-$), 2.84–1.66 (m, 4, $-SO_2CH_2CH_2CH_2-$). Repeated crystallization of the product from cyclohexane gave an analytical sample, mp 98–99°.

Anal. Calcd for $C_{10}H_{11}ClO_2S$: C, 51.93; H, 4.76; S, 13.89; Cl, 15.37. Found: C, 52.14; H, 4.90; S, 13.62; Cl, 15.56.

Benzyl Sulfoxide.—The above general oxidative procedure was used with benzyl sulfide (2.00 g, 9.34 mmol) in CH_2Cl_2 (12 ml) at −40° and sulfuryl chloride (1.31 g, 9.70 mmol) in CH_2Cl_2 (5 ml)

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

with a reaction time of 30 min at −40° and overnight at −78°. Addition of 95% ethanol (15 ml) and work-up as above gave 2.13 g (99%) of crude benzyl sulfoxide, mp 115–120°. The crude product was free of benzyl sulfide and benzyl sulfone by nmr analysis and when the solid was washed with some hexane gave 1.88 g (88%) of pure benzyl sulfoxide: mp 133–134° (lit.[11] mp 135–136°); nmr ($CDCl_3$) δ 7.34 (s, 10, aromatic H's), 3.87 (s, 4, $-CH_2-$). The nmr spectrum was identical with that of an authentic sample.

Phenyl Sulfoxide.—Reaction of phenyl sulfide (1.0 g, 5.4 mmol) and sulfuryl chloride (0.80 g, 5.9 mmol) in CH_2Cl_2 (9 ml) at −30 to −40° for 90 min produced a yellow precipitate, hydrolysis of which, with 95% ethanol (10 ml) and usual work-up, gave 1.04 g (95%) of crude phenyl sulfoxide, mp 63–67°. The crude material was washed with a small amount of hexane and provided 0.57 g (53%) of pure phenyl sulfoxide: mp 68–70° (lit.[11] mp 69–71°); ir ($CHCl_3$) 1033 cm^{-1} (>S=O) [lit.[11] 1033 cm^{-1} (>S=O)].

Phenyl Methyl Sulfoxide.—Thioanisole (1.0 g, 8.1 mmol) in CH_2Cl_2 (1 ml) and sulfuryl chloride (1.09 g, 8.0 mmol) in CH_2Cl_2 (10 ml) were mixed and kept at −70° for 2 hr. Hydrolysis of the resulting yellow solution with 95% ethanol (15 ml) followed by the usual work-up gave 1.09 g (96%) of phenyl methyl sulfoxide: mp 29–30° (lit.[11] mp 29–30°); ir (CCl_4) 1050 cm^{-1} (>S=O) [lit.[11] 1050 cm^{-1} (>S=O)]; nmr ($CDCl_3$) δ 7.70–7.33 (m, 5, aromatic H's), 2.73 (s, 3, $-SOCH_3$). Nmr analysis showed that the product was free of thioanisole and phenyl methyl sulfone.

Ethyl *n*-Octadecyl Sulfoxide.—Employing the general oxidation procedure, ethyl *n*-octadecyl sulfide (603 mg, 1.92 mmol) and sulfuryl chloride in CH_2Cl_2 (15 ml) were allowed to react at −60° for 24 hr. The reaction mixture was treated with 95% ethanol (10 ml) and standard work-up gave 0.50 g (80%) of ethyl *n*-octadecyl sulfoxide, mp 75–76° (dried by azeotropic distillation of H_2O with benzene), ir ($CHCl_3$) 1010 cm^{-1} (>S=O). An analytical sample, mp 78.5–79.5°, was prepared by recrystallization from ether and dried over P_2O_5 at 65° for 2 days. The sulfoxide is hygroscopic.

Anal. Calcd for $C_{20}H_{42}OS$: C, 72.66; H, 12.81. Found: C, 72.88; H, 12.79.

Ethyl *n*-Octadecyl Sulfone.—A mixture of *m*-chloroperbenzoic acid (0.80 g, 4.6 mmol) and ethyl *n*-octadecyl sulfoxide prepared from ethyl *n*-octadecyl sulfide (1.21 g, 3.8 mmol) and sulfuryl chloride (0.59 g, 4.4 mmol) was stirred in $CHCl_3$ (5 ml) at room temperature for 1 day. After the reaction mixture was filtered and the solvent removed from the filtrate, the residual oil was chromatographed on alumina (A-540) and upon elution with benzene gave 1.2 g (90%) of ethyl *n*-octadecyl sulfone, mp 85–86°, ir ($CHCl_3$) 1300 and 1130 cm^{-1} (>SO_2).

Anal. Calcd for $C_{20}H_{42}O_2S$: C, 69.30; H, 12.22. Found: C, 69.11; H, 12.18.

Tetramethylene Sulfoxide.—Sulfuryl chloride (15.8 g, 0.117 mol) in CH_2Cl_2 (5 ml) was added to a solution of tetramethylene sulfide (10 g, 0.114 mol) in CH_2Cl_2 (20 ml) and the mixture was allowed to stand at −70° for 3 days. The reaction mixture was treated with 80% ethanol (20 ml) and allowed to warm up to room temperature. The aqueous solution after neutralization of the reaction mixture with potassium carbonate was concentrated prior to extraction with $CHCl_3$. After the $CHCl_3$ extract was dried and the solvent was removed, distillation of the residue (7.1 g) gave 6.0 g (50%) of tetramethylene sulfoxide, bp 48–53° (0.15–0.20 Torr). The product was identified by comparison of nmr and ir spectra with those of an authentic sample.

Low-Temperature Nmr Measurements.—The nmr spectra of 2,3-dihydro-1-benzothiepin,[28] 1-methoxy-2,3-dihydro-1-benzothiepinium fluoroborate (**12**), and the intermediate from the reaction of sulfuryl chloride and 2,3-dihydro-1-benzothiepin were obtained at −50° on a Varian HA-60 nmr spectrometer equipped with a variable temperature probe. The chemical shifts were measured using TMS as an internal standard.

A 0.2-ml aliquot of a 2.5 *M* 2,3-dihydro-1-benzothiepin (**10**)[28] stock solution in $CDCl_3$ was mixed with 0.1 ml of $CDCl_3$ and cooled to −50°. To this solution was added a 0.2-ml aliquot of 2.5 *M* sulfuryl chloride in $CDCl_3$ mixed with 0.1 ml of $CDCl_3$ precooled to −50°. The resulting yellow solution was shaken vigorously with cooling and placed in the nmr probe at −50°.

The chemical shifts for these compounds are summarized in Table II.

Registry No.—**2**, 41947-71-1; **4**, 21609-60-9; **5**, 41947-73-3; **6**, 41947-74-4; **8**, 26524-92-5; **8** 2,4-dinitrophenylhydrazone, 41947-76-6; **10**, 21609-62-1; **11**, 41947-78-8; **12**, 41947-79-9; **14**, 41947-80-2; 3,4-dihydro-1-benzothiepin-5(2*H*)-one, 21609-70-1; 5-hydroxy-2,3,4,5-tetrahydro-1-benzothiepin, 20500-27-0; ethyl *n*-octadecyl sulfoxide, 41947-83-5; ethyl *n*-octadecyl sulfide, 41947-84-6; sulfuryl chloride, 7791-25-5; ethyl *n*-octadecyl sulfone, 41947-85-7; *m*-chloroperbenzoic acid, 937-14-4.

Reactions of Thiopyrylium Cations with Amines

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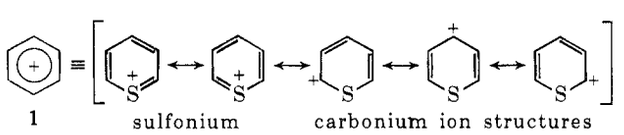
The reactions of parent thiopyrylium cation (**1**) with various primary amines under mild conditions give ring-opening products, 5- (alkyl- or arylamino-) *N*-alkyl- or -aryl-2,4-pentadienylideniminium salts (**4**) in good yield. Secondary amines also react with **1** to afford the same type of products. No reaction of 2,4,6-triphenylthiopyrylium cation with aromatic amines took place.

As recently reported[1] SCF MO calculations show that the positive charge in thiopyrylium cation (**1**) is largest at the sulfur atom (+0.854), but still considerable at the carbon atoms of the α and the γ positions (+0.080 and +0.039, respectively), indicating that **1** can be expressed as a resonance hybrid of sulfonium structures (Kekulé structures) and carbonium ion structures.



Little work has been carried out on the reaction of the parent thiopyrylium cation (**1**) with nucleophilic reagents. Price, *et al.*,[2] reported that the reaction of **1** and 2,4,6-triphenylthiopyrylium cation (**2**) with phenyllithium gave thiabenzene derivatives by nucleophilic attack at the sulfur atom. In the case of phosphopyridinium salt, water also reacts preferentially at the heteroatom, rather than carbon.[3] In contrast, we found[4] that the reaction of **2** with a variety of active methylene compounds in the presence of a base yielded substituted benzenes by nucleophilic attack of the carbanions at the α carbon atom. Attempts to isolate

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(4) Z. Yoshida, S. Yoneda, H. Sugimoto, and T. Sugimoto, *Tetrahedron*, **27**, 6083 (1971).