

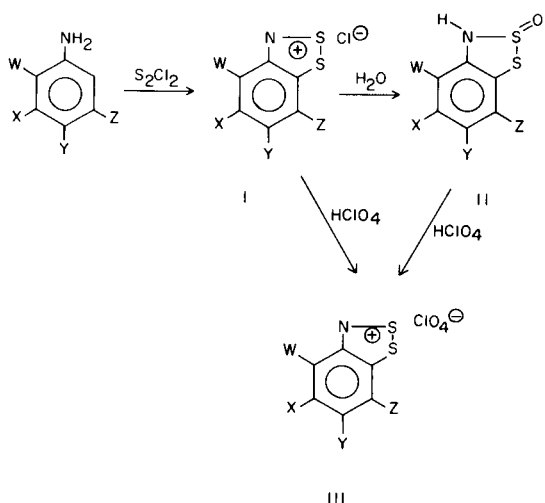
## 1,3,2-Benzothiazathiolium Perchlorates

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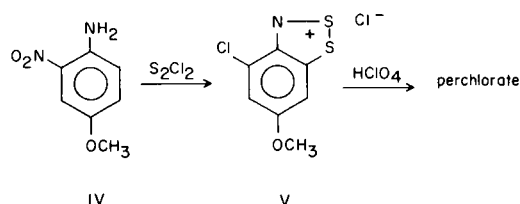
Recently, a number of papers have discussed the mechanism of the reaction of sulfur monochloride with aromatic amines (Herz Reaction) and the structure and properties of the resulting 1,3,2-benzothiazathiolium halides (1-7).

In addition to halide salts, 1,3,2-benzothiazathiolium fluoroborates and perchlorates can be synthesized in good yield from the hydrolysis product (II) of the corresponding benzothiazathiolium chloride (I) (6).



These fluoroborate and perchlorate salts are generally easily purified whereas the simple halide salts are not. It now has been found that direct exchange of perchlorate for the halide anion is often simpler than formation of the fluoroborate or the synthesis of the perchlorates via the benzodithiazole oxide (II). This method appears to be the best general method for the synthesis of stable, pure benzothiazathiolium salts. Data on a number of such perchlorate salts are given in Table I. All of these salts were obtained by converting the appropriate aromatic primary amine to the benzothiazathiolium chloride (and then to the perchlorate) by a simple reaction with sulfur monochloride except the isomeric chloro-, methoxy-

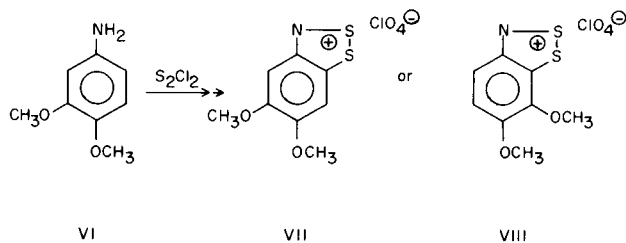
benzothiazathiolium chlorides. In these salts, the ring substituted chloro group was introduced by replacement of a nitro group (e.g. IV  $\rightarrow$  V).



The replacement of a nitro group *ortho* or *para* to the amino group is very easily accomplished and has been noted frequently (8).

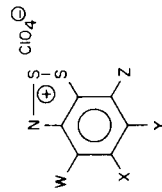
In certain instances, the perchlorates prepared by direct exchange (I  $\rightarrow$  III) resisted purification by crystallization from hot acetic acid. In some of these cases, the desired pure perchlorate was obtained via the oxide route (I  $\rightarrow$  II  $\rightarrow$  III). The data on the new 1,2,3-benzodithiazole 2-oxides which were synthesized during the course of perchlorate formation, is summarized in Table I. Each of these oxides showed a characteristically strong IR band at 8.9-9.2  $\mu$  which is due to the  $S=O$  group in this system.

In the synthesis of 5,6-dimethoxybenzothiazathiolium perchlorate (also the corresponding 5,6-dichloro-salt), two isomeric products are possible (VII and VIII). The NMR spectrum of the product shows two aromatic hydrogens



at about 1.8  $\tau$  with only very slight splitting ( $J < 1$  cps). This low coupling constant is characteristic of hydrogens *para* to each other thus indicating that formula VII is correct (9).

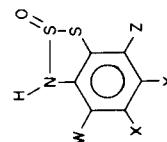
TABLE I  
1,3,2-Benzothiazathiolium Perchlorates



W	X	Y	Z	m.p. (dec.), °C	Color	Yield, % (a)	Formula	Calcd., % C H N	Found, % C H N	Ultraviolet Spectral Data $\lambda$ max (m $\mu$ )	log $\epsilon$
H	H	Cl	H	199-202	brown	66	C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> NO <sub>4</sub> S <sub>2</sub>	25.01 1.05	25.25 1.09	365, 420	4.18, 3.69
H	H	OCH <sub>3</sub>	H	186-188.5	brown	66	C <sub>7</sub> H <sub>6</sub> ClNO <sub>5</sub> S <sub>2</sub>	29.63 2.13 4.94	29.80 2.19 4.90	370, 440	3.93, 4.04
H	H	OC <sub>2</sub> H <sub>5</sub>	H	157-159	brownish orange	45	C <sub>8</sub> H <sub>8</sub> ClNO <sub>5</sub> S <sub>2</sub>	32.27 2.71	32.08 2.73	370, 442	3.95, 4.05
H	H	OCH <sub>2</sub> $\phi$	H	174.5-177	dark red	58	C <sub>13</sub> H <sub>10</sub> ClNO <sub>5</sub> S <sub>2</sub>	43.40 2.80	43.14 2.60	371, 442	3.95, 4.09
H	H	SCH <sub>3</sub>	H	233-237	dark green	30	C <sub>7</sub> H <sub>6</sub> ClNO <sub>4</sub> S <sub>3</sub>	28.04 2.02 4.67	28.20 2.10 4.85	263(s), 283(s) 392, 516, 605(s)	3.85, 3.80, 3.58, 4.30, 3.18
H	H	$\phi$	H	229-231	red	78	C <sub>12</sub> H <sub>8</sub> ClNO <sub>4</sub> S <sub>2</sub>	43.71 2.44	43.53 2.58	271, 313, 412, 490	4.08, 3.51, 3.95, 4.21
H	H	COOCH <sub>3</sub>	H	249-251	brownish yellow	59	C <sub>8</sub> H <sub>6</sub> ClNO <sub>6</sub> S <sub>2</sub>	30.83 1.94	31.15 2.04	349, 426	4.25, 3.28
H	H	COOC <sub>2</sub> H <sub>5</sub>	H	220-221	yellow	36 & 33 (b)	C <sub>9</sub> H <sub>8</sub> ClNO <sub>6</sub> S <sub>2</sub>	33.15 2.52 4.29	33.18 2.48 4.30	350, 426	4.24, 3.28
H	H	NH $\phi$	H	225.5-226	black	74	C <sub>12</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	41.80 2.63 8.12	41.70 2.76 8.30	288, 337 356(s), 520	3.96, 3.72, 3.67, 4.30
Cl	H	Cl	H	222-223.5	orange	29 (b)	C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> NO <sub>4</sub> S <sub>2</sub>	22.34 0.63 4.34	22.49 0.80 4.42	368, 461	4.21, 3.63
Cl	H	OCH <sub>3</sub>	H	225-230	reddish brown	22	C <sub>7</sub> H <sub>5</sub> Cl <sub>2</sub> NO <sub>5</sub> S <sub>2</sub>	26.42 1.58 4.40	26.59 1.70 4.50	260, 381, 464	3.98, 4.03, 3.91
Cl	H	OC <sub>2</sub> H <sub>5</sub>	H	209.5-211.5	orange	36	C <sub>8</sub> H <sub>7</sub> Cl <sub>2</sub> NO <sub>5</sub> S <sub>2</sub>	28.92 2.12 4.22	28.84 1.99 4.19	261, 381, 463	3.94, 4.05, 3.93
OCH <sub>3</sub>	H	Cl	H	224-226	dark purple	15	C <sub>7</sub> H <sub>5</sub> Cl <sub>2</sub> NO <sub>5</sub> S <sub>2</sub>	26.42 1.58 4.40	26.62 1.72 4.24	261, 365, 527	4.23, 4.19, 3.69
H	Cl	Cl	H	201-205	brownish red	36 (b)	C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> NO <sub>4</sub> S <sub>2</sub>	22.34 0.63	22.13 0.70	378, 429(s), 540(s)	4.20, 3.40, 2.55

W	X	Y	Z	m.p. (dec.), °C	Color	Yield, % (a)	Formula	Calcd., % C H N	Found, % C H N	Ultraviolet Spectral Data $\lambda$ max (m $\mu$ )	log $\epsilon$
H	OCH <sub>3</sub>	OCH <sub>3</sub>	H	215-217	greenish black	32	C <sub>8</sub> H <sub>8</sub> ClNO <sub>6</sub> S <sub>2</sub>	30.63 2.57	30.53 2.35	270(s), 415	3.63, 4.25
OCH <sub>3</sub>	H	Cl	Cl	220-221	dark violet	52 (b)	C <sub>7</sub> H <sub>4</sub> Cl <sub>3</sub> NO <sub>5</sub> S <sub>2</sub>	23.84 1.14	23.63 1.09	269, 367, 562	4.23, 4.12, 3.64
				264-266	red	45	C <sub>10</sub> H <sub>6</sub> ClNO <sub>4</sub> S <sub>2</sub>	39.54 1.99	39.54 2.03	286, 315(s), 412, 486	4.16, 3.18, 4.13, 3.34
				232-234	greenish brown	70	C <sub>10</sub> H <sub>5</sub> Cl <sub>2</sub> NO <sub>4</sub> S <sub>2</sub>	35.52 1.49	35.70 1.43	297, 329, 475	3.83, 3.96, 4.09

## 3H-1,2,3-Benzodithiazole 2-Oxides



W	X	Y	Z	m.p. (dec.), °C	Yield, %	Formula	Calcd., % C H N	Found, % C H N
H	H	COC <sub>2</sub> H <sub>5</sub>	H	124-125	65	C <sub>9</sub> H <sub>9</sub> NO <sub>3</sub> S <sub>2</sub>	44.43 3.73 5.76	44.56 3.90 5.90
H	Cl	Cl	H	105-106.5	87	C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> NO <sub>3</sub> S <sub>2</sub>	30.01 1.25	29.98 1.30
OCH <sub>3</sub>	H	Cl	Cl	147.5-148.5	83	C <sub>7</sub> H <sub>5</sub> Cl <sub>2</sub> NO <sub>2</sub> S <sub>2</sub>	31.12 1.86	31.00 1.83

(a) Yield based on aromatic primary amine. (b) Via the oxide route.

## EXPERIMENTAL

All melting points were determined on a Fisher-Johns apparatus and are uncorrected. The elemental analyses were done by Galbraith Laboratories, Inc.; Knoxville, Tennessee. The ultraviolet spectra were taken with a Beckman DB Spectrophotometer using redistilled trifluoroacetic acid as solvent.

General Method for the Synthesis of the 1,3,2-Benzothiazathiolium Perchlorates.

Twenty millimoles of the purified aromatic amine were dissolved in 25 ml. of glacial acetic acid. To this solution was added 10 ml. (120 mmoles) of sulfur monochloride. The resulting mixture was stirred at room temperature for 1/2 hour and then at 70-75° for 3 hours. After the mixture was cooled to room temperature, 25 ml. of dry benzene was added and the mixture filtered. The benzothiazathiolium chloride precipitate was washed with dry benzene, dry ether, and then dried in a vacuum to constant weight.

Direct Exchange.

One to two mmoles of the crude chloride was heated with 5 to 50 ml. of glacial acetic acid (depending on the solubility of the chloride). If any insoluble material remained, it was removed by filtration. To the hot solution (or filtrate) was added 6 drops (ca. 2.8 mmoles) of 72% perchloric acid. This mixture was stirred at room temperature for one hour and then diluted with a volume of dry ether equal to the original volume of the acetic acid. The mixture was filtered, the crystalline precipitate washed with dry ether, and dried in a vacuum.

For purification of the perchlorate, it was dissolved in a minimum amount of hot glacial acetic acid and allowed to cool slowly. The crystalline product was collected, washed, and dried as before.

Via the Oxide.

The procedure used was essentially the same as the method previously described (3,6).

No problem was encountered with explosions during the synthesis or melting point determination of the perchlorates. However, all of the perchlorates explode when heated considerably above their melting point.

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