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The Synthesis of 1,3,2-Benzothiazathiolium Salts by the Dehydration of 3*H*-1,2,3-Benzodithiazole 2-oxides (I)

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The formation of derivatives of the 1,3,2-benzothiazathiolium cation (I) by treatment of a variety of aromatic primary amines with sulfur monochloride was reported by R. Herz in 1922 (2). More recently the cation I has been synthesized in high yield by treatment of the appropriately substituted 2-amino-benzenethiol hydrochloride with thionyl chloride (3).

By this latter method, the parent Herz compound, 1,3,2-benzothiazathiolium chloride could be synthesized. This is not possible by the method of Herz because of nuclear chlorination in the 6 position which always accompanies the reaction of aniline with sulfur monochloride (4,5,6). The major drawback of both of the preceding methods is that they give only the chloride salt of I. Unfortunately the chloride salts are unstable and difficult to purify. Only 6-phenylbenzothiazathiolium chloride has been purified to the point where it gives a satisfactory analysis (7). The method of purification used in this instance does not appear to give good results with other Herz compounds.

The problem of the synthesis of stable salts of the

benzothiazathiolium system appears to be solved by the use of benzodithiazole 2-oxides (III) which can be readily obtained in good yield by purification of the hydrolysis products of Herz compounds (3). It was found that these oxides readily dissolve in strong acids to form brightly colored solutions which are similar in color to acidic solutions containing cation I. In studying this reaction further, it was found that the oxides (III) readily dissolved in a mixture of boron trifluoride-diethyl etherate and 50% hydrofluoric acid to give yellow to red solutions from which was precipitated crystalline I fluoroborates in 58-89% yield. When the parent oxide (III; X and Y = H) was treated with perchloric acid a similar reaction led to the formation of a stable benzothiazathiolium perchlorate. Unlike the chlorides, both the fluoroborates and the perchlorate can be crystallized from hot acetic acid to give products which give good elemental analyses (see Table I). The conversion of the oxides (III) to cation I probably involves the dehydration in the sequence shown as III, IV, I.

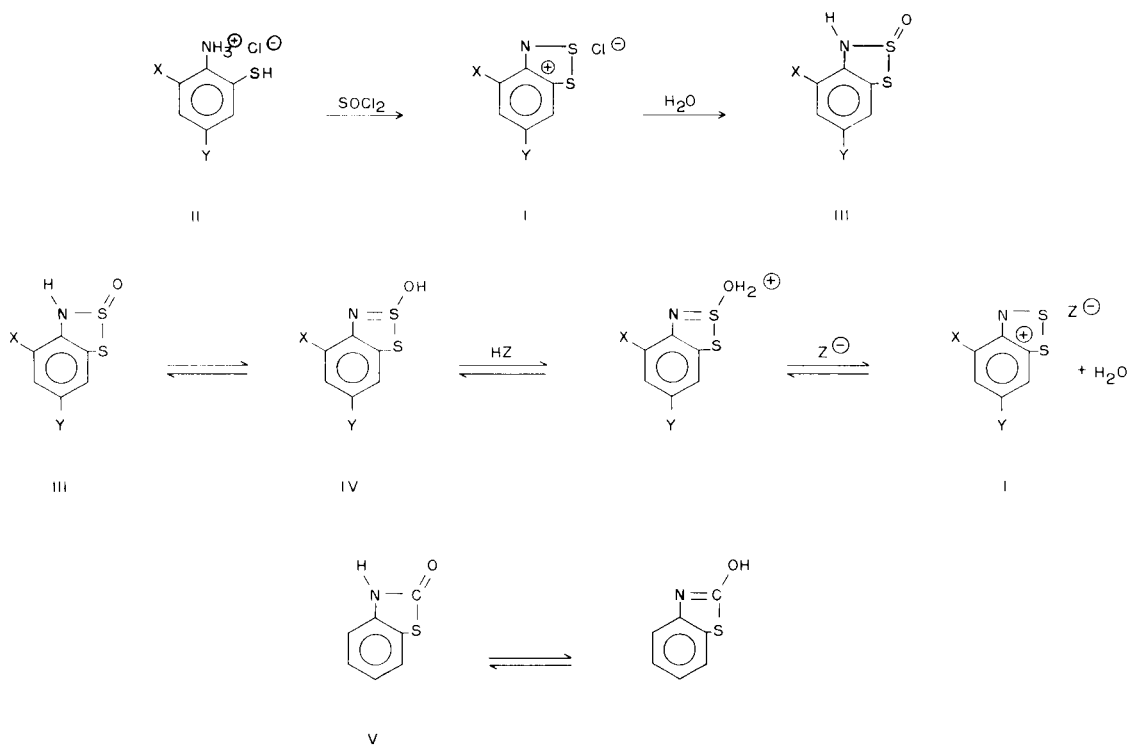
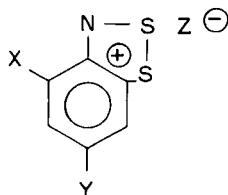


TABLE I

1,3,2-Benzothiazathiolium Salts



X	Y	Z	M. p. (dec.), °C	Yield, %	Calcd., %			Found, %		
					C	H	N	C	H	N
H	H	BF ₄	165-166.5	86	29.90	1.67	5.81	29.94	1.68	5.90
H	Cl	BF ₄	163-165	58	26.16	1.10	5.08	26.41	1.24	5.23
Cl	Cl	BF ₄	203-208	89	23.25	0.65	4.52	23.47	0.81	4.69
H	H	ClO ₄	209-211	78	28.41	1.59	5.52	28.64	1.41	5.48

TABLE II

Ultraviolet Spectral Data

X	Y	Z	λ max (m μ)	log ϵ
H	H	BF ₄	344	4.15
			423	3.28
H	Cl	BF ₄	366	4.18
			419	3.70
Cl	Cl	BF ₄	367	4.20
			461	3.63
H	H	ClO ₄	344	4.15
			424	3.26

It is known that the tautomeric equilibrium between III and IV greatly favors III (3) just as the equilibrium between 2-benzothiazolone (V) and its tautomer favors V (8). However, it is likely that the dehydration actually involves protonation of the "enol" tautomer (IV) in the same manner that acid catalyzed dehydration of ordinary alcohols involves initial protonation of the hydroxyl group. To investigate the extent of conversion of III to I in a strongly acidic medium, the ultraviolet spectra of I and III in trifluoroacetic acid were determined. Trifluoroacetic acid was used since both the salts (I) and the oxides (III) are soluble in this medium without giving other complicating reactions. The fact that the ultraviolet spectrum (Figure I, Table I, and ref. 3) of benzodithiazole 2-oxide in trifluoroacetic acid is entirely different from the spectrum of the same compound in 95% ethanol and that the spectrum in trifluoroacetic acid is identical with the spectrum of benzodithiazolium fluoroborate (or perchlorate) indicates that the oxide has undergone essentially quantitative dehydration in the strong acid medium. The sub-

stituted oxides (III) show a similar behavior in trifluoroacetic acid. Thus, it appears that the oxides (III) should be convenient precursors to a variety of relatively stable 1,3,2-benzothiazathiolium salts. This in turn should facilitate further investigation into this interesting heterocyclic system and such investigations are presently being pursued in this laboratory.

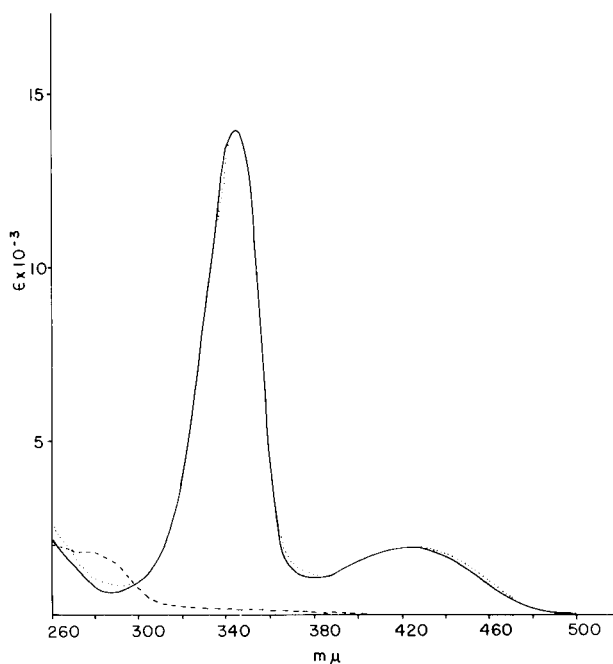


Figure I

—————	Benzothiazathiolium Fluoroborate in CF ₃ COOH
.....	Benzodithiazole 2-oxide in CF ₃ COOH
- - - - -	Benzodithiazole 2-oxide in 95% ethanol

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 95% ethanol or redistilled trifluoroacetic acid as solvent.

1,3,2-Benzothiazathiolium Fluoroborate.

To 1.04 g. (0.0061 moles) of 3*H*-1,2,3-benzodithiazole 2-oxide was added 25 ml. (0.23 moles) of redistilled boron trifluoride-diethyl etherate. After the oxide had dissolved to give a dark orange solution, 30 drops (calcd. 1 ml. --0.025 mole) of a 50% aqueous hydrofluoric acid solution was added. The resulting solution was stirred for 5 hours during which time a crystalline precipitate formed. After adding 35 ml. of anhydrous diethyl ether, the mixture was filtered and the bright yellow solid was washed with dry ether and then dried to give 1.27 g. (86%) of the fluoroborate salt, m.p. 164-167°, dec. The salt was obtained in the form of slender yellow blades with a melting point of 165-166.5°, dec., by ordinary recrystallization of 1 g. of salt from a solution of 20 ml. of acetic acid and 6 drops of 50% fluoroboric acid; infrared spectrum (KBr) (μ), 3.22w, 6.30w, 6.60w, 6.96m, 7.40m, 7.52w, 7.97w, 8.9-10.0vs, 12.25s, 12.94s, 13.72m, 14.30w.

6-Chloro-1,3,2-benzothiazathiolium Fluoroborate.

The procedure for the synthesis of the substituted fluoroborate salts was the same as above. See Table I for experimental results: infrared spectrum (KBr) (μ), 3.21w, 6.20w, 6.37s, 6.62m, 6.98w, 7.10s, 7.42m, 7.54m, 7.99w, 8.9-10.0vs, 10.46m, 11.42m, 12.10s, 12.99w, 13.26s, 15.11w.

4,6-Dichloro-1,3,2-benzothiazathiolium Fluoroborate.

Infrared spectrum (KBr) (μ), 3.21w, 6.20w, 6.36s, 6.70m, 7.05m, 7.14m, 7.42m, 7.60m, 8.23m, 8.75w, 9.0w, 9.2-10.0 vs, 10.83w, 11.22m, 11.61w, 13.27s, 13.49w.

1,3,2-Benzothiazathiolium Perchlorate.

To a stirred solution of 65.9 mg. (0.384 mmole) of the oxide in 3.5 ml. of glacial acetic acid was added 10 drops of 72% perchloric acid (calcd. 4 mmoles). After 1.5 hours the bright yellow mixture was filtered and the product was washed with anhydrous cold glacial acetic acid followed by anhydrous ether. After drying, the yield of bright yellow perchlorate was 75.7 mg. (78%), m.p. 209-211°, dec. The perchlorate can be crystallized from glacial acetic acid to give yellow needles which have the same melting point. This salt explodes when heated above its melting point.

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