atoms of (II), which were incorporated into the calculation of the R factor (with fixed positional parameters and $B_{iso} = 4.0$ Å^2). We did not locate the hydrogen atoms in (III). The intensity statistics did not unambiguously define the space group of (III). Since refinement in the $P2_1/m$ space group led to unusually short $N-O$ bond lengths we continued refinement in the $P2_1$ space group to R = 0.059, where all bond lengths had more reasonable values.

Table 2 summarizes the atomic coordinates. The structures of (II) and (III) with bond lengths and angles are shown in Figs. 1 and 2.
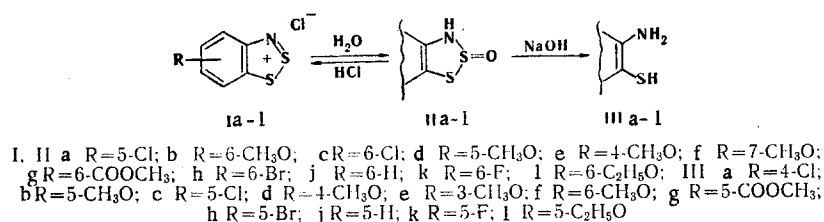
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HYDROLYSIS OF 1,2,3-BENZODITHIAZOLIUM SALTS

AND THEIR SELENIUM ANALOGS

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1,2,3-Benzodithiazolium salts (Ia)–(Il) readily react with water, forming 3H-1,2,3-benzodithiazole 2-oxides (IIa)–III) [1, 2]. Alkali readily converts (IIa)–(III) to corresponding o-aminothiophenols (IIIa-(IIII).

I, II a R=5-Cl; b R=6-CH₃O; cR=6-Cl; d R=5-CH₃O; e R=4-CH₃O; f R=7-CH₃O; g R=6-COOCH₃; h R=6-Br; j R=6-H; k R=6-F; l R=6-C₂H₅O; III a R=4-Cl; b R=5-CH₃O; c R=5-Cl; d R=4-CH₃O; e R=3-CH₃O; f R=6-CH₃O; g R=5-COOCH₃; h R=5-Br; j R=5-H; k R=5-F; l R=5-C₂H₅O

Thus sulfoxides (II) can be considered as cyclic products of the acylation of o-aminothiophenols (III) by sulfurous acid.

Table 1 summarizes the PMR parameters of 5-chloro- and 6-chloro-3H-1,2,3-benzodithiazole 2-oxides (IIa) and (IIc). Their PMR spectra plainly differ markedly from those of the cations (Ia) and (Ic). The signals of the aromatic protons are shifted upfield by 1–2 ppm in the sulfoxides relative to the cations. The 4-H and 6-H protons of sulfoxides (IIa) and (IIc) lie upfield of the 5-H and 7-H protons and of the protons of benzene itself (by 0.14–0.26 ppm), which should logically be attributed to the electron-donating effect of the nonaromatic heteroring. The sulfoxides lack the much higher downfield shift of the α-protons (4-H and 7-H) which is typical of the cations, implying that there is no ring current in the sulfoxide heteroring.

In addition to the splitting of the signals of the benzene ring protons in the synthetic sulfoxides by ortho, meta, and para coupling (Table 1) the PMR spectrum of compound (IIa) in methanol shows additional splitting of the signals of all the aromatic protons— 0.4 Hz for the 4- and 6- protons and 0.2 Hz for the 7-proton (Fig. 1). This can be due only to the existence of the sulfoxides as stereoisomers in which the $N-H$ and S=O bonds lie on the same and on different sides of the plane of the benzene ring.

TABLE 1. PMR Spectra of 1,2,3-Benzodithiazolium Salts (Ia) and
(Ic) in Trifluoroacetic Acid and of 3H-1,2,3-Benzodithiazole 2-Oxides
(IIa) and (IIc) in Methanol

Compound	Chemical shifts, δ, ppm				Coupling constants, J, Hz				
	4-H	5-H	6-H	7-H	$J_{4,5}$	$J_{6,7}$	$J_{4,6}$	$J_{5,7}$	$J_{4,7}$
Ia	8,93	—	8,43	8,83	—	9,0	2,0	—	—
Ic	9,00	8,32	—	9,00	9,5	—	—	1,5	—
IIa*	7,13	—	7,05	7,37	—	8,0	2,0	—	0,5
IIa'†	7,15	—	7,07	7,38	—	8,0	2,0	—	0,5
IIa"	7,11	—	7,03	7,36	—	8,0	2,0	—	0,5
IIc	7,01	7,13	—	7,33	8,4	—	—	1,8	0,6

*In MeOH after acidification.
†(IIa') and (IIa") are different stereoisomers of the sulfoxide.
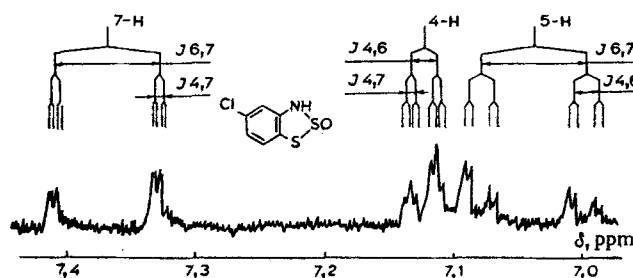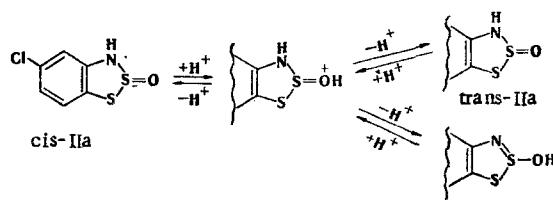

Fig. 1. PMR spectrum of 5-chloro-3H-1,2,3-benzodithiazole
2-oxide in methanol.

Acidification of a methanolic solution of compound (IIa) with trifluoroacetic acid causes the additional splitting of the signals of the benzene ring protons to disappear, apparently as a result of the fast exchange processes concomitant on protonation of the sulfoxide:

The acidity of the methanolic solutions of the sulfoxide was insufficient for the formation of significant amounts of the benzodithiazolium cation, since we detected no changes in the electronic spectrum of the solution. Under these conditions decomposition of the sulfoxides does not occur either, since addition of the resulting solution to concentrated sulfuric acid generated salt (Ia) quantitatively (from the electronic spectrum).

Though sulfoxides (IIa) and (IIb) are hydrolyzed to o-aminothiophenols in neutral and weakly acidic solutions, the reaction is far slower than in alkaline solution and the products are oxidized to the disulfides, which we isolated and identified by independent synthesis.

The electronic spectra of sulfoxides (IIa)–(III) in strongly acidic solution (70-100% H_2SO_4) are stable and identical to those of their cations (Ia)–(II). Sulfoxides (II) are thus the conjugate bases of the benzodithiazolium cations. Support for this is provided by the presence of an isosbestic point in the electronic spectra of their solutions in sulfuric acid of various concentrations (Fig. 2), which means that the irreversible side reactions can be neglected within the time of attainment of the cation (I) ⇌ sulfoxide (II) equilibrium.

We decided on a quantitative study of these prototropic reactions. We measured the electronic spectra of compounds (I) and (II) in sulfuric acid with various values of the acidity function H'_R. We calculated the basicity constants of the sulfoxides with the acidity function defined for the ionization of triarylcarbinols in aqueous sulfuric acid, since this process (like that in question here) proceeds in two stages and is accompanied by loss of water. We calculated the basicity constants from the equation $pK_a = \lg\dfrac{\varepsilon - \varepsilon_s}{\varepsilon_c - \varepsilon} + H'_R$, where ε_s, ε_c, and

TABLE 2. Basicity Constants of 3H-1,2,3-Benzodithiazole 2-Oxides (IIa)-(III)

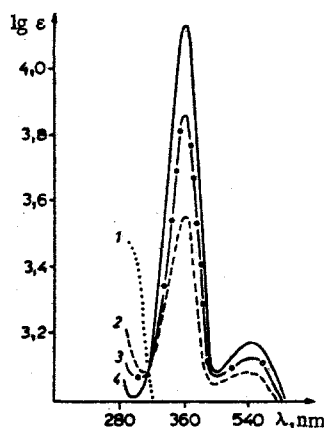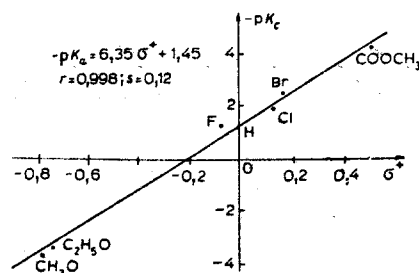| Compound	IIg	IIh	IIc	IIj	IIk	III	IIb	IIa	IIe	IId	IIf
R	6-COOCH₃	6-Br	6-Cl	6-H	6-F	6-C₂H₅O	6-CH₃O	5-Cl	4-CH₃O	3-CH₃O	7-CH₃O
% H₂SO₄	39,5	27,0	21,4	16,5	15,2	—	—	24,9	7,2	3,5	17,0
pK_a	−4,40	−2,55	−2,03	−1,46	−1,28	3,30	3,50	−2,45	−0,37	0,13	−1,51
σ⁺	0,489	0,150	0,114	0	−0,073	−0,744	−0,764				

Fig. 2   Fig. 3

Fig. 2. Electronic absorption spectra of solutions of 5-chloro-3H-1,2,3-benzodithiazole 2-oxide (IIa) (c 5×10^{-5} mole/liter) in mixtures of sulfuric acid and water; H_2SO_4 concentration: 1) 0%; 2) 24%; 3) 27%; and 4) 50%.

Fig. 3. Correlation of the basicity constants of 3H-1,2,3-benzodithiazole 2-oxides (IIb), (IIc), and (IIg)-(III) with the resonance constants σ^+ of the 6-substituents.

ε are respectively the molar absorption coefficients of the sulfoxide, cation, and their mixtures at the analytical wavelength. We found that pK_a remains constant in the experimental acidity range to within ±10% (Table 2). They correlate best with the resonance constants σ^+ of the substituents in position 6; the equation is $-pK_a = 6.35\sigma^+ + 1.45$ (r = 0.998; s = 0.12) (Fig. 3).

These considerations imply that the electron-donating substituents in position 6 of salts (I) are in direct polar conjugation with the reaction center. The reaction of formation and consequently of hydrolysis of salts (I) is extremely sensitive to the substitution ($\rho = 6.35$) though its effect is transmitted through a system of two condensed rings.

We examined the effect of the position of the substituents in the condensed benzene ring on the acid—base properties of salts (I) and prepared all the isomeric cations containing a methoxy group, (Ib), (Id), (Ie), and (If). Comparison of these four salts on the basis of the hydrolysis constants (Table 2) reveals that the electron-donating effect of the methoxy group increases in the order 7-CH_3O < 4-CH_3O < 5-CH_3O < 6-CH_3O. This is not in total agreement with the results of quantum-chemical calculations, which suggest that the electron density on the carbon atoms falls in the order 7-CH_3O > 5-CH_3O > 4-CH_3O > 6-CH_3O [4]. Thus position 5 is in stronger conjugation with the hetero ring in the reaction state than in the static state described in the calculation. The experimental basicity constants of 5-methoxy- and 5-chloro-3H-1,2,3-benzodithiazole 2-oxides (IId) and (IIa) are much higher than those calculated from the above correlation equation using the σ_{meta} substituent constants. The inapplicability of the σ_{meta} constants implies that there is a considerable contribution from the conjugated structure with charge transfer to position 5 (IV).

The existence of this sort of conjugation is supported by analysis of the electronic spectra of these compounds. The extinction of the long-wavelength band in the electronic spectra can be considered as a measure of the probability of the electronic transition. In the methoxy-substituted (I) it increases in the order 7-CH_3O < 4-CH_3O < 5-CH_3O < 6-CH_3O, which is identical to that derived from their hydrolysis constants.

The hydrolysis of the selenium analogs of the Herz salts has several distinctive features. The 1,2,3-benzothiaselenazolium cations (Va)-(Vc) and 1,2,3-benzodiselenazolium cations (VIa)-(VIc) are relatively stable in aqueous acetic acid, being hydrolyzed only when sodium acetate is added, whereas their sulfur equivalents (Ia)-(Ic) are completely hydrolyzed in dilute sulfuric acid. Careful hydrolysis of salts (Va)-(Vd) generates only intensely colored selenium-containing substances instead of compounds (VII), the analogs of sulfoxides (II). Thus the 6-chloro-1,2,3-benzothiaselenazolium salt (Vc) forms the violet compound (VIII), which is identical to the product of the reaction of 6-methoxy-1,2,3-benzothiaselenazolium chloride (Vd) with 2,2'-diamino-5,5'-dichlorodiphenyl disulfide (IX).

IV   va-d   VI   VII

a R=H; b R=5-Cl; c R=6-Cl; d R=6-CH₃O

Vc   VIII   Vb
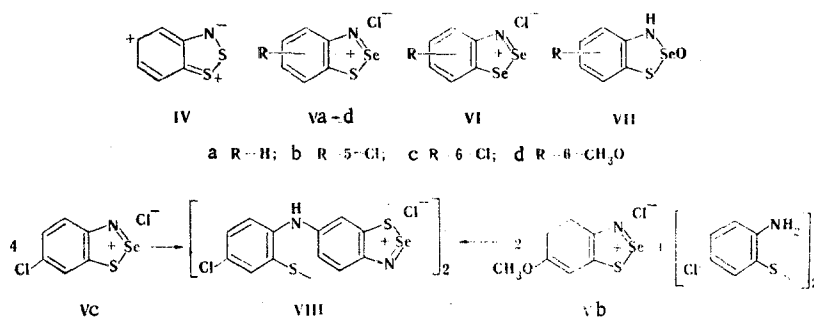
This also happens when the acidity of aqueous solutions of salts (VI) is reduced. These results imply that the intermediates, like sulfoxides (II), are extremely unstable and on mild hydrolysis form o-aminothio(seleno)-phenols, which react with the original cation to form products of nucleophilic substitution and subsequent oxidation of the type of (VIII).

Hydrolysis of 2,1,3-benzothiaselenazolium salts (Xa)-(Xc) generates diaminodiphenyl diselenides (XIa)-(XIc), which are apparently formed as a result of oxidation of the o-aminoselenophenols (XIIa)-(XIIc). In this as in the previous case the intermediate sulfoxide (XIII) undergoes rapid hydrolysis.

Xa-c   XIII a-c   XIIa-c   XIa-c

X-XIII a R=H; b R=CH₃O; c R=Cl
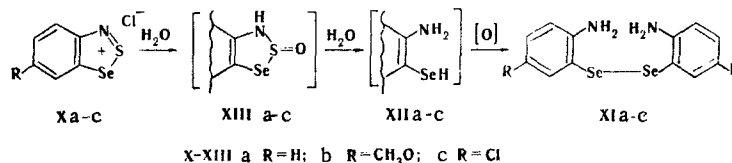
The formation of sulfoxides (XIII) in the course of the reaction is indirectly supported by the reaction of replacement of sulfur in cations (X) by selenium [2].

EXPERIMENTAL

Spectra were recorded on: UV: an SF-8 as 0.25×10^{-4} M solutions in methanol and sulfuric acid; and PMR: a Varian HA-100 (100 MHz) in trifluoroacetic acid and methanol with methylene chloride as internal standard. The homogeneity of the synthetic salts were monitored by thin-layer chromatography on Silufol in formic acid—acetic acid (1:1).

Chlorides (Ib), (Ic), (Ig), (Ih), and (Il) were prepared by the Herz reaction from the substituted anilines, chlorides (Ia), (Id), (Ie), (If), (Ij), and (Ik) by cyclization of the o-aminothiophenols with thionyl chloride [4, 6], sulfoxides (IIa)-(IIl) by the method of [7], salts (V) and (VIa)-(VId) by the methods of [2, 8], and salts (Xa)-(Xc) by the method of [9].

Hydrolysis of 5-Chloro-3H-1,2,3-benzodithiazole 2-Oxide (IIa). To sulfoxide (IIa) (mp 134-136°C; 1.02 g, 5 mmole) in methanol (50 ml) was added 10% H₂SO₄ (50 ml). The mixture was left for 3 days and then diluted with water and neutralized with sodium acetate. The precipitate was filtered off, washed with water, and dried to give 2,2'-diamino-4,4'-dichlorodiphenyl disulfide (0.3 g, 38%), mp 118°C; literature [10], mp 120°C.

The same product was obtained by this procedure after an aqueous alcohol (1:1) neutral solution has been allowed to stand, yield 75%.

Similarly 6-methoxy-3H-1,2,3-benzodithiazole 2-oxide (IIb), mp 115-118°C, gave 2,2'-diamino-5,5'-dimethoxydiphenyl disulfide (IIIb), mp 80-82°C; literature [11], mp 82°C.

Hydrolysis of 5-Chloro-1,2,3-benzothiaselenazolium Chloride (Vb). To chloride (Vb) (1.85 g, 7 mmole) in formic acid (20 ml) was added sodium acetate (80 g) in water (300 ml) with stirring. The precipitate was filtered off and crystallized from formic acid to give dithiobis[2-(benzo-1,2,3-thiaselenazolium-6-yl)amino-5-chlorobenzene] dichloride (VIII) (1.3 g, 96%), λ_{max} (log ε) 545 nm (4.43); literature [12] λ_{max} (log ε) 545 nm (4.45).

Hydrolysis of Benzo-2,1,3-thiaselenazolium Chloride (Xa). To a solution of salt (Xa) (0.5 g, 2 mmole) in formic acid (3 ml) was added a solution of sodium acetate to pH 6. The mixture was diluted to 50 ml with water. The precipitate was filtered off, dried, and crystallized from ether to give 2,2'-diaminodiphenyl diselenide (XIa) (0.3 g, 88%), mp 80°C. The compound was identical to the product of the oxidation of o-aminoselenophenol by atmospheric oxygen.

In the same way hydrolysis of 6-methoxy-2,1,3-benzothiaselenazolium chloride (Xb) gave 2,2'-diamino-5,5'-dimethoxydiphenyl diselenide (XIb) with mp 90-92°C (decomposition), identical to the oxidation product of the corresponding selenophenol.

Replacement of the Ring Sulfur by Selenium in 6-Chloro-2,1,3-benzothiaselenazolium Chloride (Xc). To chloride (Xc) (1.35 g, 5 mmole) in ethanol (10 ml) was added selenous acid (0.65 g, 5 mmole). The mixture was stirred for 5 h and then the precipitate was filtered off and crystallized from formic acid to give 6-chloro-1,2,3-benzodiselenazolium chloride (VIc) (0.4 g, 37%).

Determination of the Acid-Base Constants of Salts (Ia)-(Il) and Sulfoxides (IIa)-(IIl). The constants were measured by a spectrophotometric method. A solution (0.1 ml) of the benzodithiazole oxide (II) in methanol or of chloride (Ic) in formic acid, concentration 0.25-0.5×10^{-2} M, was transferred by pipet to sulfuric acid (10 ml) of known concentration (0.1-70%) or to citrate buffer solution (pH 2.5-4.5). Equilibrium was reached after 5-20 min at 20°C; this was monitored from the change in optical density at the absorption maximum of salt (I). Then linearity of the dependence of the optical density on the concentration of salt (I), the existence of the isosbestic point in solutions with various concentrations of sulfuric acid, and the reversibility of the reaction during the attainment of equilibrium were checked. Values of pK_α were calculated for the series of solutions (Table 2, Fig. 3).

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