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SYNTHESIS AND SOME PROPERTIES OF BENZO-1,2,3-THIASELENAZOLIUM SALTS

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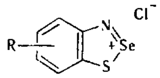
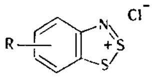
UDC 547.794.1:543.422.25

The reaction of selenious acid on benzo-1,2,3-dithiazolium salts (Herz salts) gives benzo-1,2,3-thiaselenazolium salts, which were previously obtained from o-aminothiophenols. This reaction, which involves exchange of sulfur by selenium in the heteroring, occurs only under conditions in which the products of hydrolysis of the Herz salts — benzo-3H-1,2,3-dithiazole 2-oxides — are in equilibrium with them.

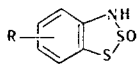
Benzo-1,2,3-thiaselenazolium salts (I) were previously obtained by reaction of selenious acid with o-aminothiophenol hydrochlorides [1]. We have found that the same heterocycles (Ia-c) are formed by the action of selenious acid on benzo-1,2,3-dithiazolium salts (IIa-c) in alcohol, acetic acid, and formic acid.



I a-e



II a-e



III a-e

I-III a R=H; b R=5-Cl; c R=6-Cl; d R=6-CH_3O; e R=6-C_2H_5O

Herz salts with donor substituents (IId,e) react in acetic and formic acids only to give admixtures of salts Id,e, which are distinctly recordable in the PMR spectra. When the acidity of the medium is reduced by the addition of sodium acetate, the reaction of IId with selenious acid in acetic acid gives Id as the final product. The 6-dimethylamino and 6-phenylamino derivatives of the Herz salt do not undergo reaction under these conditions.

Replacement of sulfur by selenium was not observed in concentrated hydrochloric and sulfuric acids or when selenium tetrabromide was used in place of selenious acid.

Thus the ability of Herz salts IIa-e to undergo reaction with selenious acetate decreases as the electron-donor properties of the substituents increase and the acidity of the medium increases. The same relationship is also observed for the ability of Herz salts to undergo hydrolysis to give benzo-3H-1,2,3-dithiazole 2-oxides (IIIa-e).

This made it possible to assume that the reaction with selenious acid does not proceed directly with the cations of II but rather through a step involving sulfoxides III. In fact, sulfoxides II react vigorously with selenious acid in acetic and formic acids to give salts I, which were isolated in the form of the chlorides. The mechanism of this transformation of sulfoxides III to cations of I remains unclear, since the assumption that the reaction proceeds through a step involving prior nucleophilic opening of the heterorings of III under the influence of a protic solvent or selenious acid is not in agreement with the fact that this transformation can also be carried out in aprotic media (by the action of selenium dioxide on IIIc,d in anhydrous dimethylacetamide, acetonitrile, nitrobenzene, and xylene). Nevertheless, the possibility of the preparation of salts I directly from

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Leningrad Branch, All-Union Scientific-Research Institute of Synthetic Fibers. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1361-1364, October, 1976. Original article submitted May 23, 1975; revision submitted February 18, 1976.

TABLE 1. Chemical Shifts* and Spin–Spin Coupling Constants

Compound	Chemical shifts, ppm				SSCC, Hz				
	4-H	5-H	6-H	7-H	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	$J_{4,6}$	$J_{5,7}$
I a	8.81	8.12	8,44	8.69	9	6,5	9	2	2
II a	8.98	8,34	8,54	8,93	8.8	7	8,5	1,2	1.2
I b	8.75	—	8.35	8,61	—	—	9,5	1.9	—
II b	8,83	—	8,43	8.83	—	—	9,2	1,8	—
I c	8.71	8.71	—	8,71	9.5	—	—	—	1
II c	9.00	8.32	—	9,00	9.5	—	—	—	1.8
I d	8.54	7.71	4,26*	8.09	9,8	—	—	—	2.2
II d	8.70	7.88	4.31*	8.24	9.8	—	—	—	2.2
I e	8.49	7.66	4,52*	8,06	9.5	—	—	—	2.2

*These are the chemical shifts of the protons of the substituents.

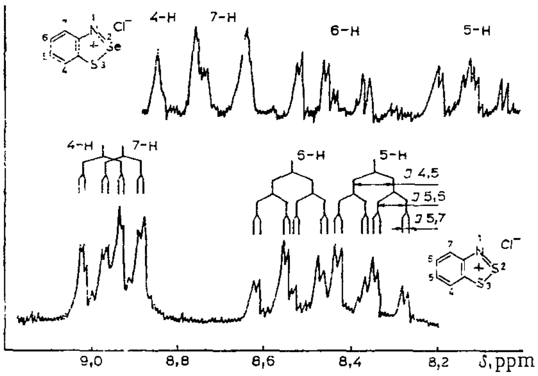
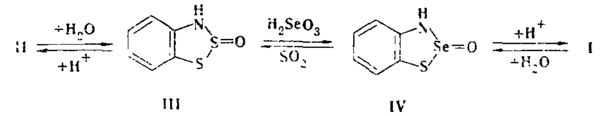


Fig. 1. PMR spectra of benzo-1,2,3-thiaselenazolium (Ia) and benzo-1,2,3-dithiazolium (IIa) chlorides.

Herz salts in good yields makes them readily accessible. The use of sulfoxides III makes it possible to obtain salts I with various anions, for example, in the form of acetates, formates, chlorides, etc. One should note the much higher resistance to hydrolysis of salts I as compared with Herz salts II.

In our opinion, the reaction involving exchange of sulfur by selenium proceeds as follows:



Under the reaction conditions, equilibrium IV⇌I is shifted completely to favor cation I in view of its higher stability.

The signals of aromatic protons corresponding to three-spin systems of the ABC type (Ib-e) and of a four-spin system of the ABCD type (Ia) were observed in the PMR spectra of salts Ia-e (Fig. 1). The PMR spectra of Ia and IIa are similar to the spectrum of the previously described benzo-1,2,3-diselenazolium chloride, and this makes it possible to interpret them within the first-order approximation [2] with an accuracy of ± 2 Hz. The signals in the spectra of unsubstituted Ia and IIa were assigned on the basis of the spectra of Ib, c and IIb, c. The spectral parameters of these salts are presented in Table 1.

As in the case of benzodiselenazolium salts, an increase in the chemical shifts of the protons in the order 5-H, 6-H, 7-H, 4-H is characteristic for Ia and IIa. The α-H signals are found at weaker field than the β-H signals for Ia and IIa by ~0.5 ppm, and this indicates the substantial and comparable magnetic anisotropies of the heterorings of salts Ia and IIa. The character of the spectra is satisfactorily explained if one also takes into account the conjugation of the heteroring with the benzene ring in accordance with the scheme

The chemical shift of the 4-H proton relative to the 7-H proton and of the 6-H proton relative to the 5-H proton for Ia are shifted to weak field more markedly than in the case of Herz salt IIa, and this is particularly

TABLE 2. Benzo-1,2,3-thiaselenazolium and Benzo-1,2,3-dithiazolium Chloride

Compound	mp, °C (dec.)	Empirical formula	Found, %			Calc., %			λ_{max} (lg ε)	Yield, % (method)
			Cl	N	S	Cl	N	S		
Ia	128—136	$C_6H_4ClNSSe$	14,8	6,2	13.6	15,0	5,9	13.5	450 (3,20), 375 (4,05)	80(B)
IIa	170—178								430 (3,24.) 350 (4,08)	
Ib	180—186	$C_6H_3Cl_2NSSe$	25.7	4.9	11.4	26,1	5.2	11.8	470 (2,92), 380 (4.04)	84(A)
IIb	190—193								440 (3.18), 360 (4,61)	
Ic	230—238	$C_6H_3Cl_2NSSe$	26.0	5.0	11.6	26,1	5,2	11.8	450 (3,42), 392 (3.90)	76(A)
IIc	169—176								427 (3,61), 370 (4,06)	
Id	210—215	$C_7H_6ClNOSSe$	13.5	5.4	12,0	13,3	5,2	12.0	475 (3,92), 400 (3,86)	62(A)
IId	168—176								447 (3.87), 376 (3.84)	
Ie	230—233	$C_8H_8ClNOSSe$	12.8	5,2	11.5	12,6	5,0	11.4	475 (3.96), 400 (3,85)	58(A)
IIe	160—167								450 (3.95), 370 (3.81)	

the case for the 6-H proton; this indicates the greater degree of transfer of the positive charge to these positions in selenium analog Ia. If the delocalization of the positive charge in the benzene ring in salts I is greater than in salts II, one might expect a shift of the signals of the protons to weak field on passing from II to I. However, the reverse effect is actually observed: one sees a greater degree of shielding of the protons of Ia-e (by ~0.2 ppm). This is evidently associated with the smaller effect of the ring currents, since the benzene ring is distinguished by its even greater disruption of the equalization of bonds of the quinoid type.

The electronic spectra of concentrated sulfuric acid solutions of the compounds (Table 2), which are similar in character to the absorption bands observed for Ia-e and IIa-e, also indicate stronger conjugation of the condensed rings in I. However, the long-wave absorption band corresponding to transfer of positive charge to the substituent in the 6 position is shifted bathochromically in the spectra of salts Ia-e as compared with the corresponding band of salts IIa-e by 20-30 nm [3].

EXPERIMENTAL

The PMR spectra of trifluoroacetic acid solutions of the compounds were recorded with a Varian HA-100 spectrometer with an operating frequency of 100 MHz. The internal standard was cyclohexane (δ 1.44 ppm). The electronic spectra of solutions of the compounds in 93% sulfuric acid were recorded with an SF-8 spectrophotometer.

Benzo-1,2,3-dithiazolium salts IIc-e were obtained by the Herz reaction, and IIa, b were obtained from o-aminothiophenols and thionyl chloride [4, 5].

Synthesis of Benzo-1,2,3-thiaselenazolium Chlorides (I). A) From o-aminothiophenol derivatives. A 1.42-g (0.011 mole) sample of selenious acid was added with stirring and cooling to 0.01 mole of the hydrochloride of the appropriate o-aminothiophenol in 10 ml of 99.7% formic acid, and the mixture was stirred for 30 min. The resulting precipitate was removed by filtration and washed with 10 ml of formic acid, and 80 ml of absolute ether was added to the filtrate. The precipitate was removed by filtration, washed with ether, and vacuum dried to give benzo-1,2,3-thiaselenazolium chlorides Ib-e.

B) From benzo-1,2,3-dithiazolium chlorides. A 2.85-g (0.022 mole) sample of selenious acid was added to 0.02 mole of salts IIa-d in 10 ml of ethanol and 20 ml of acetic acid, and the mixture was stirred for 4 h. The resulting crystalline precipitate was removed by filtration and crystallized from formic acid and acetic anhydride to give benzo-1,2,3-thiaselenazolium chlorides Ia-d.

C) From benzo-3H-1,2,3-dithiazole 2-oxides, IIa-c. A 1.3-g (0.01 mole) sample of selenious acid was added with stirring and cooling with ice water to 0.01 mole of the sulfoxides in 30 ml of acetic or formic acid, and the mixture was stirred for 30 min. Ether (30 ml) was added, and the precipitate was removed by filtration and crystallized from formic acid and ether by the addition of 5 ml of a solution of hydrogen chloride in acetic acid. The product was washed with ether to give benzo-1,2,3-thiaselenazolium chlorides Ia-e.

The salts were identified from their electronic spectra and PMR spectra.

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REARRANGEMENT OF 10-ARYLSULFONYLPHENOTHIAZINES

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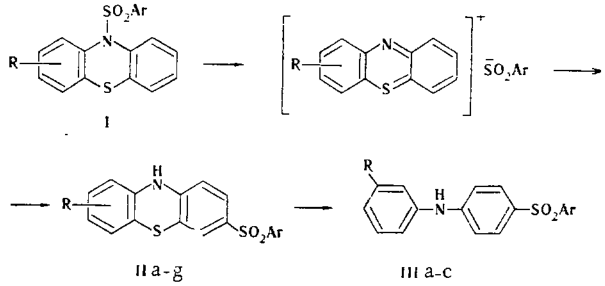
UDC 547.867.6:542.952

10-Arylsulfonylphenothiazines undergo rearrangement to 3-substituted phenothiazines on heating. The structure of the reaction products was proved by alternative synthesis and conversion to diarylamines.

A number of papers devoted to the use of substituted phenothiazines as stabilizers for petroleum products and various polymers [1] have appeared in recent years. In a search for an analogy with oxygen-containing heterocycles – 10-arylsulfonylphenoxazines [2] – we studied the behavior of 10-arylsulfonylphenothiazines (I) on heating in polar solvents.

It was observed that II are formed in high yields when 10-substituted phenothiazines I are heated to 130°C in DMF for 20-30 h. The IR spectra of II are similar to the spectra of starting methoxy- and chloro-substituted phenothiazines that do not have substituents in the 10 position; the 700-1600 cm^{-1} regions of skeletal vibrations of the rings of the N-substituted and corresponding unsubstituted phenothiazines differ appreciably. The alternative synthesis of IIb, accomplished by the method in [3], makes it possible to prove that the products are 3-arylsulfonyl-substituted phenothiazines.



I, II a $R=H$, $Ar=C_6H_5$; b $R=H$, $Ar=C_5H_4CH_3$; c $R=H$, $Ar=C_6H_4Cl$, d $R=H$, $Ar=2\text{-}C_{10}H_7$, e $R=Cl$, $Ar=C_6H_5$; f $R=Cl$, $Ar=C_6H_4CH_3$; g $R=OCH_3$, $Ar=C_6H_5$
III a $R=H$, $Ar=C_6H_5$; b $R=H$, $Ar=C_6H_4CH_3$; c $R=Cl$, $Ar=C_6H_4CH_3$

The signals of one of the condensed rings in the PMR spectrum of IIa assume the form of an ABC system with spin–spin coupling constants (SSCC) that correspond to the literature data [4]; in addition, the signal of an NH group appears (8.02 ppm).

The rearrangement probably proceeds with the intermediate formation of the phenothiazonium salt of an arenesulfinic acid; attack on the strongly electrophilic phenothiazonium cation by the sufficiently nucleophilic arenesulfinate ion in the quinogenic position relative to the nitrogen atom leads to the formation of the 3-arylsulfonylphenothiazine (II). It was established that the introduction of an electron-donor substituent – a methoxy group (Ig) – in one of the quinogenic positions relative to the nitrogen atom appreciably reduces the yield of product as compared with the yield of chlorine-containing phenothiazone (Ie, f).

When the 3 and 7 positions in I are occupied by methoxy groups, the arylsulfonyl group is split out under the given conditions. 3-Methoxy- and 3,7-dimethoxyphenothiazines were obtained by fusion of the appropriate diphenylamine with sulfur in the presence of catalytic amounts of iodine.

F. É. Dzerzhinskii Dnepropetrovsk Chemical-Engineering Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1365-1367, October, 1976. Original article submitted August 6, 1975; revision submitted March 15, 1976.