REACTIONS OF DISUBSTITUTED (IN THE PHENYL RING) ARYLTHIOLANIUM AND ARYLTHIANIUM SALTS WITH AMINES

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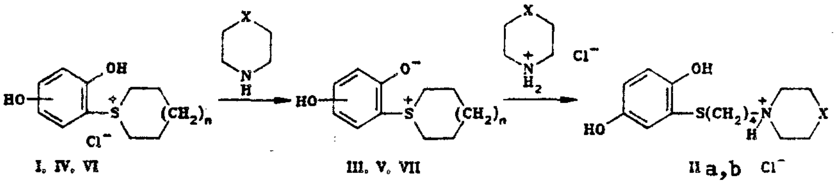
UDC 547.818'825'829.07

The reactions of 2(3)-methyl-4-hydroxy- and 2,4-dihydroxyphenylthiolanium salts with excess secondary amine (piperidine, morpholine) lead to the corresponding aryl aminobutyl sulfides. The amino sulfides formed on the basis of 2,5-dihydroxyphenylthiolanium and -thianium salts are unstable and require rapid treatment with acetic anhydride or HCl. The reaction of 2,4-dihydroxyphenylthiolanium and 2,5-dihydroxyphenylthianium salts with an equimolar amount of amine makes it possible to isolate the intermediate zwitterionic phenoxides.

It has been previously shown [1] that the hydrochloride or, respectively, the perchlorate of 4-hydroxyphenyl 4-piperidinobutyl sulfide is formed in good yield in the reaction of 4-hydroxyphenylthiolanium chloride or perchlorate with an equimolar amount of piperidine.



I, III 5-OH, $n=0$; IIa $X=CH_2$, b $X=O$; IV, V 4-OH, $n=0$; VI, VII 5-OH, $n=1$

The corresponding amino sulfide chlorides IIa, b are also formed in lower yields (even in the case of prolonged heating of the mixture of reagents in ethanol) in the reaction of equimolar amounts of piperidine or morpholine with 2,5-dihydroxyphenylthiolanium chloride (I). It might be assumed that a zwitterion and the amine hydrochloride are formed initially in this case and that amino sulfide salts II are the products of their reaction; competitive oligomerization of the zwitterion, which is known to proceed with opening of the heteroring [1], also takes place. The hypothetical intermediate – the 5-hydroxy-2-phenoxidothiolanium zwitterion* (III) – is formed in the percolation of a solution of the hydrate of salt I through an anion-exchange resin and gradually oligomerizes (with opening of the heteroring) on storage. The freshly prepared zwitterion III is monomeric in solution, and it forms 2,5-dihydroxy-phenylthiolanium perchlorate or chloride when treated with perchloric or hydrochloric acid; this constitutes evidence that an unopened thiolanium ring is present in its molecule.

Compounds II are formed when freshly obtained zwitterion III is heated with an alcohol solution of piperidine or morpholine hydrochloride; this confirms the reaction pathway presented above.

In contrast to 4-hydroxyphenylthiolanium salts [1], an amino sulfide salt could not be isolated in the reaction of 2,4-dihydroxyphenylthiolanium chloride (IV) with an equimolar amount of piperidine; only zwitterion V* was obtained (it was obtained in maximum yield when the reaction was carried out at room temperature).

Zwitterion V is converted to an infusible form when it is recrystallized from methanol. A similar form was also obtained when a solution of salt IV was percolated through an anion-exchange resin. The reaction of zwitterion V with hydrochloric or perchloric acid leads, respectively, to 2,4-dihydroxyphenylthiolanium chloride (IV) or the perchlorate.

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*We did not establish which of the two OH groups forms the phenoxide; splitting out of a proton from the hydroxy group in the 2 position is more likely.

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow 117371. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1552-1558, November, 1988. Original article submitted February 5, 1986; revision submitted April 25, 1988.

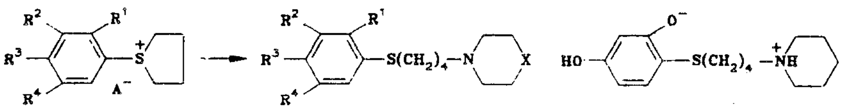
The reaction of arylthianium salts with an equimolar amount of an amine has not been previously investigated; however, it is known [2] that thianium cations are much more stable than thiolanium cations. In fact, an amino sulfide salt is not formed in the reaction of 2,5-dihydroxyphenylthianium chloride (VI) with an equimolar amount of piperidine. The reaction proceeds in different ways, depending on the solvent. An unstable complex of the hydrate of the zwitterion with piperidine hydrochloride precipitates in methanol (in the case of subsequent treatment of the reaction mixture with ether).

The presence of a thianium ring in this complex is confirmed by the results of functional analysis – by the determination of zwitterionic sulfur. This complex decomposes to give the semihydrate of the 5-hydroxy-2-phenoxidothianium zwitterion (VII) when it is heated in alcohol.

When the reaction is carried out in ethanol, the virtually pure semihydrate of zwitterion VII precipitates in high yield a few minutes after mixing of the reagents. The structure of zwitterion VII was confirmed by the results of functional analysis and mass-spectrometric data, as well as by conversion to 2,5-dihydroxyphenylthianium perchlorate by the action of perchloric acid.

A zwitterion with the same composition is formed when a solution of salt VI is percolated through an anion-exchange resin.

We have established [3] that 4-hydroxyphenylthiolanium and -thianium salts react with excess amine to give the corresponding amino sulfides. We have found that amino sulfides IXa-g (Table 1) also can be readily obtained by heating thiolanium salts IV and VIII with excess amine. Compound IXf is readily converted to a betaine on standing.



VIII a-c IX a-i X f

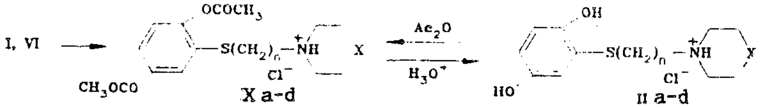
VIIIa,b IXa–c $R^1=CH_3$, $R^2=R^4=H$; VIIIc, IXd,e $R^1=R^4=H$, $R^2=CH_3$, $R^3=OH$; IXa–i $R^1=OH$, $R^2=H$; f,g $R^3=OH$, h,i $R^3=H$; f,g $R^4=H$, h,i $R^4=OH$; VIII a $A=ClO_4$, b,c $A=Cl$; IX a,d,f,h $X=CH_2$, b,e,g,i $X=O$, c $X=NH$

However, 2,5-dihydroxyphenyl aminoalkyl sulfides IXh, i could not be obtained by this method. Only dark amorphous substances, which were evidently products of further transformation of amino sulfides,* were isolated 1 h after the end of the reaction.

To obtain amino sulfides on the basis of thiolanium salt I one must first isolate their hydrochlorides IIa, b by rapid acidification of the reaction mixture with hydrochloric acid; one can use only stoichiometric amounts of the amine because of the difficulties involved in separating the salts of the amino sulfide and the amine. Bases IXh, i are isolated by passing the hydrochlorides through an anion-exchange resin. Amino sulfides IXh, i (particularly IXh) are unstable in solutions.

Amino sulfides or their hydrochlorides cannot be obtained from thianium salts with stoichiometric amounts of amine. The heteroring is not opened when salt VI is refluxed with 2 moles of the amine in alcohol; the semihydrate of the 5-hydroxy-2-phenoxidothianium zwitterion (VII) is formed at room temperature.

The reaction in a medium of the amine with subsequent rapid acetylation is a successful method for obtaining 2,5-dihydroxyphenyl ω-aminoalkyl sulfides that is also suitable for the synthesis on the basis of thianium salts. The resulting diacetates X (Table 2) are readily saponified to give amino sulfide hydrochlorides (for example, IIa-d; Table 3).



X a-d II a-d

II, X a,b $n=4$, a,c $n=5$; a,c $X=CH_2$; b,d $X=O$

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*Judging from the composition and functional and mass-spectral analysis, the amino sulfide (for example, IXh) reacts with excess amine with the formation of, presumably, 4-piperidino-5-hydroxyphenyl 4-piperidinobutyl sulfide.

TABLE 1. Disubstituted (in the Phenyl Ring) Aryl 4-Aminobutyl Sulfides IXa-i

Compound	mp,* °C	Reaction time,† h	Found, %				Empirical formula	Calc., %				Yield, %
			C	H	N	S‡		C	H	N	S	
IXa	109...111	4 (13)	69,1	9,1	5,3	11,6	$C_{16}H_{25}NOS$	68,9	9,0	5,0	11,5	53 (89)
IXb	113,5...115	6 (10)	64,1	8,1	4,6	11,3	$C_{15}H_{23}NO_2S$	64,0	8,2	5,0	11,4	66 (80)
IXc	138...144,5	9,5	64,3	8,6	9,0	11,5	$C_{15}H_{24}N_2OS$	64,2	8,6	9,9	11,4	68
IXd	106...108	3,5	68,9	8,7	5,3	11,6	$C_{16}H_{25}NOS$	68,8	9,0	5,0	11,5	69
IXe	65...68	5,5	64,1	8,2	4,7	11,4	$C_{15}H_{23}NO_2S$	64,0	8,2	5,0	11,4	91
IXf	74...84 (dec.)	9	64,1	8,2	4,8		$C_{15}H_{23}NO_2S$	64,0	8,2	5,0		56
IXg	115...116	6	59,6	7,4	4,8	11,9	$C_{14}H_{21}NO_3S$	59,3	7,5	4,9	11,3	67
IXh	98...104	—	63,6	8,0	4,3	11,2	$C_{15}H_{23}NO_2S$	64,1	8,2	4,9	11,4	20
IXi	105...110	—	58,8	7,4	4,9		$C_{14}H_{21}NO_3S$	59,2	7,4	5,0		87

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*Compounds IXa, b, d, g were crystallized from benzene.

†For IXa, b the reaction times and yields with perchlorate VIIIa are given in parentheses.

‡In the case of IXe, h sulfide sulfur was determined by titration of a solution of a sample in acetic anhydride with perchloric acid in the presence of mercuric acetate by the method in [4].

TABLE 2. Characteristics of Acetoxy-Substituted Amino Sulfide Hydrochlorides Xa-f

Compound	mp,* °C	Found, %					Empirical formula·HCl	Calc., %					Yield, %†
		C	H	Cl	N(N')	S		C	H	Cl	N	S	
X a	150...152	56,7	6,9	8,8	3,3 (3,37)		$C_{19}H_{27}NO_4S$	56,8	7,0	8,8	3,4		94 (60)
X b	165...166	53,3	6,9	8,7	3,1 (3,40)		$C_{18}H_{25}NO_5S$	53,6	6,4	8,8	3,5		(95)
X c	170...172	57,8	7,2	8,2	3,2	7,5	$C_{20}H_{29}NO_4S$	57,8	7,2	8,5	3,4	7,7	96
X d	167...169	53,9	6,9	8,5	3,1	7,7	$C_{19}H_{27}NO_5S$	54,6	6,8	8,5	3,3	7,7	80
X e	198...201	56,9	7,1	9,6	3,4 (4,0)	9,4	$C_{17}H_{25}NO_3S$	56,7	7,2	9,9	3,9	8,9	27
X f dihydrate	oil	57,8	8,6		3,5	6,7	$C_{23}H_{37}NO_5S$	58,0	8,1		2,9	6,7	89
Xg‡	oil	67,2	8,4	—	—	—	$C_{18}H_{27}NO_2S$	67,2	8,4	—	—	—	95

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*Compound Xa was crystallized successively from acetic acid and acetone; Xe was crystallized from methanol.

†The yields of the products of acetylation of hydrochlorides IIa, b are presented in parentheses.

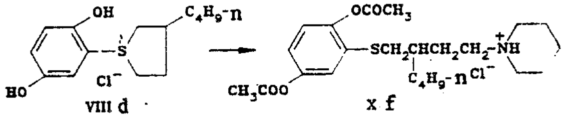
‡Amino sulfide.

TABLE 3. Amino Sulfide Hydrochlorides IIc, d and IXa-g

Compound	mp, °C	Found, %			Empirical formula·HCl	Calc., %			Yield, %
		Cl	N	S		Cl	N	S	
IIa	141...143	10,5	3,7	9,9	$C_{16}H_{25}NO_2S$	10,7	4,2	9,7	70
IIb dihydrate	78...80	9,7	3,3	9,6	$C_{16}H_{29}NO_4S$	9,6	3,8	8,7	80
IId	136...137	10,1	3,9	9,8	$C_{15}H_{23}NO_3S$	10,6	4,2	9,6	72
IXa	155...157	11,6	4,2	10,9	$C_{16}H_{25}NOS$	11,2	4,4	10,2	85
IXb	102...105	11,6	4,4	10,4	$C_{15}H_{23}NO_2S$	11,2	4,4	10,1	89
IXc	200...202,5	18,9	7,8	—	$C_{15}H_{24}N_2OS$	20,0	7,9	—	68
IXd	150...151,5	11,4	3,8	—	$C_{16}H_{25}NOS$	11,2	4,4	—	62
IXe	144...145	11,0	3,7	10,3	$C_{15}H_{23}NO_2S$	11,2	4,4	10,1	89
IXg	142...144	11,3	3,7	9,8	$C_{14}H_{21}NO_3S$	11,1	4,4	10,0	65

*Compounds IXa, b, d, e-g are the amino sulfide hydrochlorides, while IXc is the dihydrochloride.

The acetylation of salts IIa, b also leads to diacetates Xa, b. The process can be realized in steps and stopped at the step involving the monoacetate (Xe). Amino sulfide diacetate hydrochloride Xf was obtained on the basis of butylthiolanium salt VIIId by a combination of the synthetic conditions found. The site of cleavage of the ring was established from mass-spectroscopic data.


VIII d

X f

EXPERIMENTAL

The mass spectra were recorded with an LKB-2091 spectrometer (250°C, 50 mA). The PMR spectrum was obtained[*] with a Varian T-60 spectrometer.

2,5-Dihydroxyphenyl(4-N-Piperidinobutyl Sulfide Hydrochloride (IIa). A) A 0.85-g (10 mmoles) sample of piperidine was added to a hot solution of 2.32 g (10 mmoles) of 2,5-dihydroxyphenylthiolanium chloride (I) in 8 ml of ethanol, and the mixture was refluxed for 6 h. The next day the precipitated crystals were separated and washed with acetone to give 1.19 g (38%) of a substance with mp 190-194°C. The wash liquid was added to the filtrate to give another 0.42 g (14%) of a substance with mp 188-190°C. Recrystallization from ethanol gave 0.72 g (32%) of amino sulfide salt IIa with mp 196-198°C. The solubilities of IIa at 20°C in various solvents were as follows: 1% in water, 0.63% in ethanol, and 2% in methanol. The product was quite soluble in DMF at ordinary temperatures and when it was heated in DMSO and sulfolane. PMR spectrum (CD_3OD): 1.77 [4H, m, $CH_2(CH_2)_2CH_2$], 3.00 4H, m, SCH_2, NCH_2), 6.65, 6.82 ppm (d, aromatic). Found, %: C 57.0; H 7.2; N 4.2; N^+ (by the method in [3]) 4.4; S 10.6. $C_{15}H_{24}ClNO_2S$. Calculated, %: C 56.7; H 7.6; N 4.4; S 10.1. Mass spectrum[*] (150°C, 12 eV): 281 $[M - HCl]^+$ (100), 248 (7.9) [M − 248 = 33 − characteristic (for sulfides) splitting out of SH as a result of a complex recombination], 197 (15.2) $[(OH)_2C_6H_3{-}S{-}(CH_2)_4{-}]$, 155 (10.2) $[(OH)_2C_6H_3{-}S^+{=}CH_2]$, 141 (84.8) $[(OH)_2C_6H_3{-}S]$, 98 (71) $[CH_2{=}N]$.

B) A solution of zwitterion III was obtained from 1.21 g (5 mmoles) of 2,5-dihydroxyphenylthiolanium chloride semihydrate in methanol on ARA-2p anion-exchange resin and added to 1.21 g (10 mmoles) of piperidine hydrochloride. The methanol was evaporated in vacuo, the residue was dissolved in ethanol, and the mixture was refluxed for 4 h. The resulting precipitate was separated and recrystallized from alcohol to give 0.85 g (54%) of hydrochloride IIa with mp 193-195°C. No melting-point depression was observed for a mixture of the samples obtained.

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[*] The authors thank V. G. Zaikin for recording and discussing the mass spectra and A. Yu. Koshevnik for recording the PMR spectrum.

[†] Here and subsequently, the m/z values (relative intensities in percent) are presented.

2,5-Dihydroxyphenyl(4-N-Morpholinobutyl Sulfide Hydrochloride (IIb). A) A 0.87-g (10 mmoles) sample of morpholine was added to a hot solution of 2.32 g (10 mmoles) of sulfonium chloride I in 10 ml of ethanol, and the mixture was refluxed for 6 h. Acetone was added to precipitate 1.80 g (56%) of hydrochloride IIb with mp 184-188°C. Recrystallization from alcohol gave a product with mp 190-191°C. The solubility in alcohol at 78°C was 4.3 g/100 ml, as compared with 0.6% at 20°C. Mass spectrum (90°C, 12 eV): 283 (100 $[M - HCl]^+$, 250 (25), 197 (5), 196 (25), 155 (12.5), 141 (35), 100 (35), 87 (12.5), 36 (7.5). Found, %: C 52.4; H 6.3; Cl 11.0; N 4.2; S 9.9. $C_{14}H_{22}ClNO_3S$. Calculated, %: C 52.5; H 6.9; Cl 11.1; N 4.4; S 10.0.

B) A solution of zwitterion III was obtained from 2.32 g (10 mmoles) of salt I in methanol on AV-17 anion-exchange resin and was added to 2.46 g (20 mmoles) of morpholine hydrochloride. The methanol was evaporated in vacuo, the residue was dissolved in ethanol, and the mixture was refluxed for 4.5 h. After 3 days, the precipitate was separated and recrystallized from 35 ml of alcohol to give 1.10 g of hydrochloride IIb with mp 189-190°C; another 0.18 g of sulfide IIb, with mp 186-190°C, was isolated from the filtrate for an overall yield of 40%. No melting-point depression was observed for a mixture of this product with a genuine sample.

5-Hydroxy-2-phenoxidothiolanium Zwitterion (III). A solution of 2.51 g (0.01 mole) of 2,5-dihydroxyphenylthiolanium chloride hydrate in 11 ml of absolute methanol was percolated through ARA-2p anion-exchange resin in the OH form (the volume of the anion-exchange resin was 26 ml, and the layer height was 34 cm). The methanol was removed from the desorbate in vacuo without heating, and the residual oil began to crystallize when it was treated with ethanol. The precipitate was removed by filtration and washed with ethanol and acetone to give 1.06 g (54%) of zwiterion III in the form of a free-flowing yellow powder with mp 114-119°C. Found, %: S 15.7; S^+ 16.7 (by the method in [3]). $C_{10}H_{12}O_2S$. Calculated, %: S 16.3. On standing the substance polymerized and underwent partial decomposition – it gradually darkened, the percentage of onium sulfur decreased, and sulfide sulfur developed. Thus, the following values were found after 2 months: S^+ 12.1% and S^+ + sulfide S 15.1%. After 7.5 months, the S^+ value found was 3.6%, and the substance was not completely soluble in methanol.

A solution of zwitterion III was obtained from 2.32 g (10 mmoles) of chloride I in methanol on 20 ml of AV-17 anion-exchange resin and added to a mixture of 2.38 g of 42% $HClO_4$ and 10 ml of acetone, and the resulting solution was concentrated in vacuo. Ether was added to the residue to precipitate 1.64 g (55%) of 2,5-dihydroxyphenylthiolanium perchlorate with mp 183-184°C. No melting-point depression was observed for a mixture of the product with a genuine sample. Another 0.04 g of the perchlorate was isolated from the mother liquor.

A solution of 2.32 g (10 mmoles) of the chloride in methanol was percolated through 10 ml of AV-17 anion-exchange resin. The desorbate was vaporized rapidly in vacuo, and the residue was acidified with hydrochloric acid to give 2,5-dihydroxyphenylthiolanium chloride hydrate, with mp 89-91°C, in 80% yield.

Perchlorate VIIIa, with mp 179-181°C, was obtained in 80.7% yield from thiolane oxide by the method in [5]. Found, %: C 45.2; H 5.1. $C_{11}H_{15}ClO_5S$. Calculated, %: C 44.8; H 5.1.

Chloride VIIIb was obtained in 59% yield by the action of potassium chloride on salt VIIIa by the methods in [5, 6].

Salts VIIIc and IV were obtained as in [6], while salts I and VI were obtained by the method in [7].*

4-Aminobutyl Aryl Sulfides IXa-g. A 10-20 mmole sample of salt VIIIa-c or IV was dissolved in the minimum amounts of methanol or alcohol, and the solution was refluxed for several hours with a tenfold excess of the amine.† The excess amine was removed by distillation in vacuo, and ether was added to the residue (or directly to the mixture). The

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*The authors thank T. A. Bardin and I. N. Degtyarev for providing us with a sample of salt VI.

†In a number of cases the reaction was carried out without a solvent, and the excess amine was not removed.

amine salt was separated, and amino sulfides IXa-g (Table 1) were isolated from the ether. Mass spectrum of IXf (70°C, 12 eV): 281 $M^{+\cdot}$, 140, 98.

3-Methyl-4-acetoxyphenyl 4-Piperidinobutyl Sulfide (Xg). This compound was obtained by heating 1 g of salt IXa at 100°C with a mixture of equal volumes of acetic anhydride and acetic acid.

The amino sulfide hydrochlorides (Table 3) were precipitated by passing dry hydrogen chloride into solutions of amino sulfides IXa-e in dry ether.

2,5-Dihydroxyphenyl 4-Aminobutyl Sulfides IXh, i. A 10-mmole sample of salt I was dissolved in 11 ml of alcohol, 20 mmoles of piperidine or morpholine was added, and the mixture was refluxed for 1 h in an inert gas atmosphere. It was then cooled and acidified rapidly with HCl—alcohol (1:1) to precipitate IXh or IXi (Table 1).

As in the case of the hydrate of I, a 0.01-mole sample of the hydrochloride of IXh or IXi was percolated through ARA-2p anion-exchange resin, and IXh or IXi was isolated from the desorbate (in the case of IXh the desorbate residue was treated with CCl_4). Mass spectrum (100°C, 12 eV) of IXh: 281 [M^+], 248, 98. Mass spectrum (150°C, 12 eV) of IXi: 283 M^+.

2,5-Diacetoxyphenyl ω-Aminoalkyl Sulfide Hydrochlorides Xa-d. A 5-mmole sample of salt I or VI was refluxed with a tenfold amount of the amine, after which the mixture was cooled, a mixture of 8.5 ml of acetic anhydride and 1.2 ml of acetic acid was added slowly dropwise with cooling, and the mixture was refluxed for 1 h. It was then concentrated in vacuo, and the acetylated amine was extracted with hexane or ether. The residue was treated with acetone to precipitate salts Xa-d (Table 2). Mass spectrum (80°C, 12 eV) of Xc: 379 [M − HCl]. Mass spectrum (80°C, 70 eV) of Xd: 381 [M − HCl], 339, 297, 295, 281, 253, 211, 156, 142, 141, 100, 87.

Hydrochlorides IIa, b were acetylated as indicated above with the formation of diacetates Xa, b. Monoacetate Xe was isolated from the reaction mixture for Xa after refluxing for 5 min.

2,5-Diacetoxyphenyl 2-(2-Piperidinoethyl)hexyl Sulfide Hydrochloride (Xf). A 3.4-mmole sample of salt VIIId was heated with piperidine for 1 h in an inert gas atmosphere, after which the mixture was acidified and evaporated, and the residue was acetylated with acetic anhydride to give salt Xf. Mass spectrum (150°C, 70 eV): 421 $[M - H_2O - HCl]^+$, 337, 155 $[Ar - CH_2]^+$, 182 $[CH(Bu)CH_2CH_2N(CH_2)_5]^+$, 112 $[CH_2CH_2N(CH_2)_5]^+$, 98 $[CH_2{=}N(CH_2)_5]^+$, 85, 70, 57.

2,5-Dihydroxyphenyl 5-Aminopentyl Sulfide Hydrochlorides IIc, d. A 2.5-mmole sample of hydrochloride Xc or Xd was refluxed in 12 ml of water and 0.44 ml of concentrated hydrochloric acid (with the addition of alcohol in the case of Xd), after which the mixture was evaporated (or treated with acetone in the case of Xd), and the solid material was recrystallized from alcohol. Salt IIc precipitated from the reaction mixture in the form of the dihydrate. Mass spectrum (100°C, 12 eV) of IIc: 295 $[M - HCl]^+$, 154, 98. Mass spectrum (100°C, 70 eV) of IId: 297 $[M - HCl]^+$, 264, 211, 156, 142, 141, 100.

4-Hydroxy-2-phenoxidothiolanium Zwitterion (V). A) A 0.37-g (4.3 mmoles) samples of piperidine was added to a solution of 1 g (4.3 mmoles) of 2,4-dihydroxyphenylthiolanium chloride (IV) in 7 ml of methanol; zwitterion V precipitated immediately. After 2 h, the zwitterion was separated to give 0.44 g (51%) of a product with mp 164-164.5°C. Found, %: C 61.4; H 6.2; S 16.5; zwitterion S^+ 15.5. $C_{10}H_{12}O_2S$. Calculated, %: C 61.2; H 6.2; S 16.3. The filtrate was evaporated, the residue was treated with methanol, and another 0.24 g of V was isolated for an overall yield of 79%; the yield of zwitterion V was only 51% in the case of refluxing for 12 h. Recrystallization from methanol gave zwitterion V with mp 173-175°C.* If a sample was heated gradually starting at room temperature, it softened at 163°C but did not melt up to 245°C. Found, %: zwitterion S^+ 16.0. $C_{10}H_{12}O_2S$. Calculated, %: S 16.3. A solution of 0.32 g (1.63 mmoles) of zwitterion V in methanol was acidified with concentrated HCl, and the mixture was evaporated. The residue consisted of 0.38 g (quantitative yield) of salt IV with mp 172-173.5°C. No melting-point depression was observed for a mixture of the product with a genuine sample.

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*The capillary containing the substance should be inserted into the block at 150°C and heated rapidly.

B) A solution of 1.16 g (5 mmoles) of salt IV in absolute methanol was percolated through 13 ml of ARA-2p anion-exchange resin. A 0.22-g sample of zwitterion V, with mp 173-175°C,* precipitated from the desorbate. Found, %: C 61.7; H 6.3; S 16.5; zwitterion S^+ 16.0. $C_{10}H_{12}O_2S$. Calculated, %: C 6.12; H 6.2; S 16.3. Another 0.4-g sample of V, which softened at 176-186°C during ordinary heating but did not melt at up to 245°C and charred at 360-380°C, was isolated from the filtrate. The overall yield of V was 63%.

A solution of zwitterion V (obtained from 0.2 g of salt IV on the anion-exchange resin) was acidified with 67% $HClO_4$, the mixture was evaporated, and the residue was treated with ether to give 0.15 g (60%) of 2,4-dihydroxyphenylthiolanium perchlorate with mp 116-118°C. Found, %: C 40.2; H 4.6. $C_{10}H_{13}ClO_6S$. Calculated %: C 40.5; H 4.4.

5-Hydroxy-2-phenoxidothianium Zwitterion (VII) Semihydrate. A) A 0.42-g (5 mmole) sample of piperidine was added to a solution of 1.32 g (5 mmoles) of 2,5-dihydroxyphenylthianium chloride (VI) hydrate in 3 ml of methanol. After 1 week, the mixture was poured into 35 ml of ether to precipitate a viscous oil, which began to crystallized after 24 h. The crystals of the complex were separated and washed with ether to give 1.52 g (87%) of a product with mp 106-110°C. Found, %: C 55.0; H 7.9; Cl 11.1; N 4.4; S 10.0. $C_{16}H_{28}ClNO_3S$. Calculated, %: C 55.0; H 8.2; Cl 10.1; N 4.0; S 9.2. Functional analysis: Found, %: N^+ 4.0; S^+ 9.1. A 134-g sample of the complex was heated with 1.9 ml of ethanol to precipitate 0.20 g (24%) of zwitterion VII. Found, %: C 60.0; H 7.0. $C_{22}H_{30}O_5S_2$. Calculated, %: C 60.1; H 6.8.

B) A 0.42-g (5 mmoles) sample of piperidine and 1 ml of ethanol were added to a slightly heated solution of 1.32 g (5 mmoles) of sulfonium chloride VI in 4 ml of ethanol; a precipitate began to form after a few minutes. The next day the precipitate was separated and washed with ethanol and acetone to give 0.66 g (90%) of zwitterion VII with mp 147°C (dec.). Found, %: C 59.8; H 6.5; S 14.5; zwitterion S^+ 14.7. $C_{22}H_{30}O_5S_2$. Calculated, %: C 60.1; H 6.7; S 14.6. The product was soluble in water, and the solution had pH 8. The solubility in hot ethanol was ~3%. Partial dehydration, oligomerization, and conversion to an infusible form (which softened at 145°C and then darkened and charred) occurred when the product was recrystallized from ethanol.

2,5-Dihydroxyphenylthianium perchlorate, with mp 229.5-230°C, precipitated in the reaction of zwitterion VII with perchloric acid in acetic acid. No melting-point depression was observed for a mixture of the product with a genuine sample. Mass spectrum of zwitterion VII (150°C, 12 eV): 210 (43.5) [M^+], 2.18 (4.7), 110 (100), 102 (58); (195°C, 12 eV): an ion peak at 420 (33) [M^+ dimer — dehydration and polymerization when the sample was introduced/appeared.

C) A solution of 1.32 g (5 mmoles) of salt VI in absolute methanol was percolated through 13 ml of ARA-2p anion-exchange resin. The desorbate was evaporated in vacuo without heating, and the powdery residue was washed with ethanol to give 0.89 g (82%) of the almost colorless zwitterion VII. On heating the substance "shrank" at 145°C and charred without melting on further heating. Zwitterion VII was soluble in methanol and acetic acid. Found, %: C 60.2; H 6.9; S 14.6; zwitterion S^+ 14.4. $C_{22}H_{30}O_5S_2$. Calculated, %: C 60.1; H 6.7; S 14.6. 2,5-Dihydroxyphenylthianium perchlorate was obtained in 77% yield in the reaction of zwitterion VII with perchloric acid.

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*See footnote previous page.