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CONDENSED HETEROAROMATIC SYSTEMS THAT INCLUDE A THIOPHENE RING

37.* PREPARATION OF ISOMERIC FORMYL-SUBSTITUTED SELENOLS OF THE BENZO[b]THIOPHENE SERIES

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Isomeric 2-formylbenzo[b]thiophene-3-selenol and 3-formylbenzo[b]thiophene-2-selenol and their sulfur analogs were obtained by nucleophilic substitution of the bromine atom in 3-bromo-2-formylbenzo[b]thiophene or the isomeric 2-bromo-3-formylbenzo[b]thiophene by a hydroselenide or hydrosulfide group by the action of an alcohol solution of NaSeH or NaSH, as well as by the action of selenourea with subsequent alkaline hydrolysis. Various Schiff bases were obtained from the isolated formyl-substituted selenols and thiols by two methods, and complexes with divalent Zn, Cd, and Ni were obtained by reaction of the Schiff bases with the corresponding metal acetates.

We have previously [1] obtained 2-formylbenzo[b]thiophene-3-selenol (I) and 3-formylbenzo[b]thiophene-2-selenol (II) by organolithium synthesis by the method developed for the analogous compounds with a sulfur atom [2]. However, in contrast to the 80% yields obtained for the analogous sulfur-containing isomers, the yields in the preparation of the selenium compounds were only 21%.

Further development of our research on the structures and properties of derivatives of isomeric formyl-substituted selenols I and II and complexes based on them required us to improve the methods for their synthesis in order to increase the yields and to decrease the amounts of side products, which hinder the synthesis and isolation of pure ligands and complexes. On the basis of the literature data we concluded that the most convenient methods are those based on nucleophilic substitution of a labile Cl or Br atom by a hydroselenide group. 3-Bromo-2-formylbenzo[b]thiophene (III) and 2-bromo-3-formylbenzo[b]thiophene (IV), which were obtained by the methods in [3] and [4], respectively, served as the starting compounds. We initially used selenourea (Method A), which judging from the data in [5], leads to the formation of selenols in good yields, as the nucleophilic agent. However, the synthesis of formyl-substituted selenols I and II by this method is accompanied by the significant formation of side products that are insoluble in alcoholic alkali solution; this can be explained by the possible condensation of the amino group of selenourea with the formyl group, as well as by nucleophilic substitution of the bromine in IV by the amino group of selenourea [4]. Nevertheless formyl-substituted selenols I and II were obtained in 40-45% yields after two reprecipitations from an alcoholic alkali solution by acidification with dilute HCl.

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* See [1] for communication 36.

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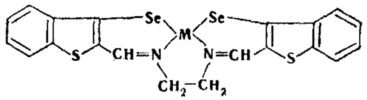
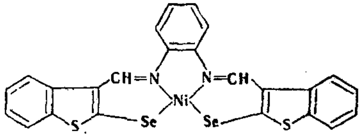
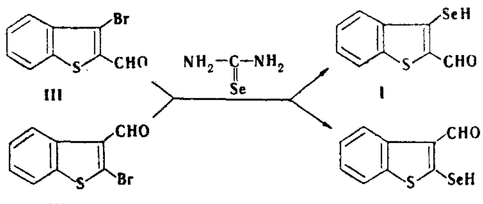
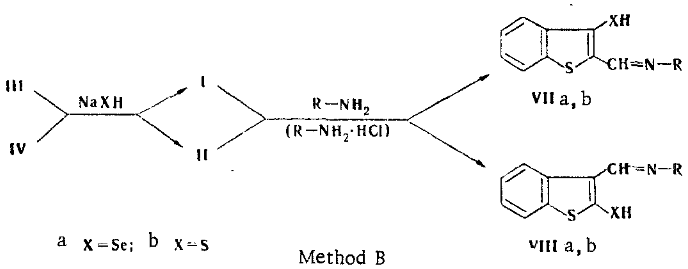
TABLE 1. Schiff Bases of Isomeric Formyl-Substituted Selenols and Their Sulfur Analogs and Complexes Formed from Them

Compound	R	M^{2+}	mp, °C	Found, %						Empirical formula	Calculated, %						Yield, %	Color
				C	H	N	S	Se	M		C	H	N	S	Se	M		
VIIa	n-C_4H_9	—	212—213	52,5	5,0	4,4	10,7	26,8	—	$C_{13}H_{15}NSSe$	52,7	5,1	4,7	10,8	26,6	—	41	Cherry-red
VIIIa	2-Naphthyl	—	211—212	62,4	3,8	3,9	8,6	21,6	—	$C_{19}H_{13}NSSe$	62,3	3,6	3,8	8,8	21,6	—	43	Red
VIIIa	m-$NO_2C_6H_4$—	—	179—181	50,0	3,0	7,5	9,0	21,9	—	$C_{15}H_{10}N_2O_2SSe$	49,9	2,8	7,8	8,9	21,9	—	42	Violet
VIIIa	1/2 (—CH_2CH_2—)	—	227—228	47,3	3,0	5,1	12,4	31,1	—	$C_{20}H_{16}N_2S_2Se_2$	47,4	3,2	5,5	12,7	31,2	—	51	Yellow
VIIb	p-$CH_3OC_6H_4$	—	172—174	64,1	4,4	4,6	21,4	—	—	$C_{16}H_{13}NOS_2$	64,2	4,4	4,7	21,4	—	—	90	Red
VIIb	2-Naphthyl	—	190—191	71,5	4,2	4,5	20,4	—	—	$C_{19}H_{13}NS_2$	71,4	4,1	4,4	20,1	—	—	86	Cherry-red
VIIIb	2-Naphthyl	—	216—217	71,3	4,1	4,2	20,3	—	—	$C_{19}H_{13}NS_2$	71,4	4,1	4,4	20,1	—	—	88	Yellow
VIIIb	H	—	160—161	57,0	3,8	7,1	33,1	—	—	$C_9H_7NS_2$	56,9	3,7	7,2	33,2	—	—	87	Yellow
		Zn	235—236	42,1	2,6	4,8	11,3	28,0	11,1	$C_{20}H_{14}N_2S_2Se_2Zn$	42,2	2,5	4,9	11,3	27,7	11,5	85	Yellow needles
		Cd	280—283 (dec.)	38,7	2,5	4,6	10,3	25,7	18,0	$C_{20}H_{14}N_2S_2Se_2Cd$	39,0	2,3	4,5	10,4	25,6	18,2	80	Yellow needles
		Ni	352—353 (dec.)	47,0	2,5	4,3	10,5	26,0	9,5	$C_{24}H_{14}N_2S_2SeNi$	47,2	2,6	4,6	10,5	25,8	9,6	76	Black needles

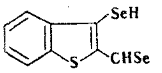


Method A

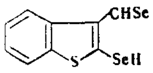
The formation of side products and the presence of ammonia (liberated in the alkaline hydrolysis step), which may lead to the formation of a selenol aldimine and dimeric products of condensation with ammonia [6], prompted us to attempt to synthesize the isomeric formyl-substituted selenols I and II by a different method (Method B), namely by using sodium hydroselenide [7] as the nucleophilic agent. The isomeric I and II were obtained in almost quantitative yields by the action of excess alcohol is sodium hydroselenide solution on the isomeric bromo aldehydes III and IV; the formation of very small amounts of selenoaldehydes V and VI was observed in this case. This is indicated by the presence in the mass spectra of I and II of an $M^{+\cdot}$ peak at m/e 304 and the fact that the results of elementary analysis for Se are too high (by 3-4%). The amounts of the indicated impurities depend on the excess amount of sodium hydroselenide used and on the rate of acidification with hydrochloric acid in the second step of the synthesis. It is known [8] that the carbonyl group is capable undergoing reaction with selenols (hydrogen selenide) to give selenoacetals, and the formation of selenoaldehydes V and VI is the result of their conversion in the acidification step. Hydrogen selenide is evolved when the reaction mixture is reprecipitated from an alcoholic alkali solution by the addition of dilute hydrochloric acid, and the reaction mixture becomes homogeneous in character.



Method B



V



VI

The reaction of bromo aldehydes III and IV with an alcohol solution of sodium hydrosulfite and subsequent treatment of the reaction mixture with excess amine hydrochlorides gave the isomeric mercapto aldimines VIIb and VIIIb (in 86-90% yields), which were previously obtained in our laboratory by the organolithium synthesis [2].

Schiff bases VIIa and VIIIa were obtained from the isomeric formyl-substituted selenols I and II by condensation with amines; the reaction of these Schiff bases with $M(OAc)_2$ gave complexes with divalent Zn, Cd, and Ni. The results are presented in Table 1.

EXPERIMENTAL

The IR spectra of KBr pellets were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Specord UV-vis spectrophotometer. The mass spectra were recorded with a Varian MAT CH-6 mass spectrometer. The molecular weights of the isomeric formyl-substituted selenols were determined with an ÉP-75 precision ebulliograph.

2-Formylbenzo[b]thiophene-3-selenol (I) and 3-Formylbenzo[b]thiophene-2-selenol (II). A) A 5-g (0.021 mole) sample of 3-bromo-2-formylbenzo[b]thiophene (III) or 2-bromo-3-formylbenzo[b]thiophene (IV) was dissolved by heating in 80 ml of methanol, 2.61 g (0.021 mole) of selenourea was added to the solution, and the mixture was stirred for 1.5 h. The solution was then acidified with dilute hydrochloric acid, and the precipitate was separated by filtration and dissolved in alcoholic alkali solution. The alkaline solution was acidified, and this operation was finally repeated. The yellow precipitate was dried in vacuo over P_2O_5 to give 2.3 g (45%) of aldehyde I with mp 115-116°C. UV spectrum: λ_{max} (C_2H_5OH) 225 nm; λ_{max} ($CHCl_3$) 243 nm. IR spectrum: 3400 cm^{-1} (OH...). Found: C 45.1; H 2.5; S 13.1; Se 32.4%. M_{ebull} 248. C_9H_6OSSe. Calculated: C 44.8; H 2.5; S 13.3; Se 32.7%. M 241. The yield of aldehyde II, with mp 137-138°C, was 40%. UV spectrum: λ_{max} (C_2H_5OH) 228 nm; λ_{max} ($CHCl_3$) 243 nm. IR spectrum: 3450 cm^{-1} (OH...). Found: C 44.6; H 2.4; S 13.8; Se 32.3%. M_{ebull} 236. C_9H_6OSSe. Calculated: C 44.8; H 2.5; S 13.3; Se 32.7%. M 241.

B) A 5.7-g (0.024 mole) sample of bromo aldehyde III or IV was added in a stream of argon to a solution of NaSeH obtained [8] by the addition of 100 ml of absolute alcohol to a mixture of 5.1 g (0.065 mole) of powdered Se and 5 g (0.132 mole) of $NaBH_4$ (the excess amount of $NaBH_4$ depends on its quality, and it is imperative that the resulting solution is not red), and the mixture was stirred at 75°C for 35-40 min. It was then cooled to room temperature, and a solution of 10 ml of concentrated HCl in 30 ml of water was added to it slowly dropwise in the course of 40 min with vigorous stirring (in a rapid stream of argon for removal of the H_2Se). The precipitate that formed after reprecipitation from alcoholic alkali solution by acidification with dilute HCl was removed by filtration and dried in vacuo over P_2O_5 to give 5.7 g of aldehyde I or 5.6 g of aldehyde II. The melting points and UV and IR spectra of I and II were in agreement with the constants of the formyl-substituted selenols obtained by method A and by the organolithium synthesis [1].

Schiff Bases of 2-Formyl-3-mercaptobenzo[b]thiophene (VIIb) and 3-Formyl-2-mercaptobenzo[b]thiophene (VIIIb). A hot solution of 2.75 g (0.012 mole) of bromo aldehyde III or IV in 150 ml of methanol was added with stirring in a stream of argon to 15 ml of a 17% methanol solution containing 2.55 g (0.035 mole) of KSH, and the mixture was heated on a water bath for 1 h. It was then cooled and treated with excess amine hydrochloride, and the precipitate was removed by filtration, washed twice with water and alcohol, and dried over P_2O_5. The results are presented in Table 1.

Schiff Bases of 2-Formylbenzo[b]thiophene-3-selenol (VIIa) and Its Isomer (VIIIa). These compounds were obtained by heating equimolar amounts of formyl-substituted selenol I or II and primary amines for 40 min in $CHCl_3$ or CCl_4; a precipitate formed after the bulk of the solvent was removed by evaporation and the concentrate was cooled. The results are presented in Table 1.

Divalent Zn, Cd, and Ni Complexes. These complexes were obtained by the addition of a solution of the metal acetate in DMF to a solution of the corresponding base in the minimum amount of hot DMF. The precipitates were removed by filtration and recrystallized from DMF. The results are presented in Table 1.

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