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RING-CHAIN TAUTOMERISM OF VINYLOGS OF 2(3)-AMINO DERIVATIVES OF HETEROCYCLIC o-HYDROXY ALDEHYDES

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Previously unknown vinylogs of 2(3)-aminomethylene-substituted benzo[b]thiophene-3-one, 1-methyloxindole, 1-methylindoxyl, benzo[b]furan-3-one, and indan-1,3-dione have been synthesized. Their tautomeric transformations have been studied by methods of UV, IR, and PMR spectroscopy. It has been shown that the introduction of a substituent into the β position of a dienic chain favors the appearance of the cyclic form.

We have previously [1] established the existence of the ring-chain tautomerism of derivatives of 2-(γ-dimethylaminopropenylidene)benzo[b]thiophene-3(2H)-one. In the present investigation we have studied the possibility of solvato-, photo-, and thermochromic transformations of vinylogs of 2(3)-aminomethylene-substituted derivatives of benzo[b]thiophene-3-one (I), 1-methyloxindole (II), 1-methylindoxyl (III), benzo[b]furan-3-one (IV), and indan-1,3-dione (V) and their acylated derivatives, and the influence of structural factors on the position of the ring-chain tautomeric equilibrium A ⇄ B.

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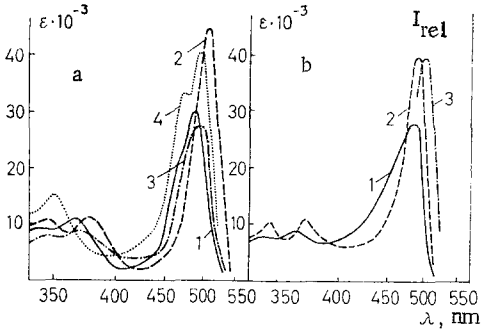


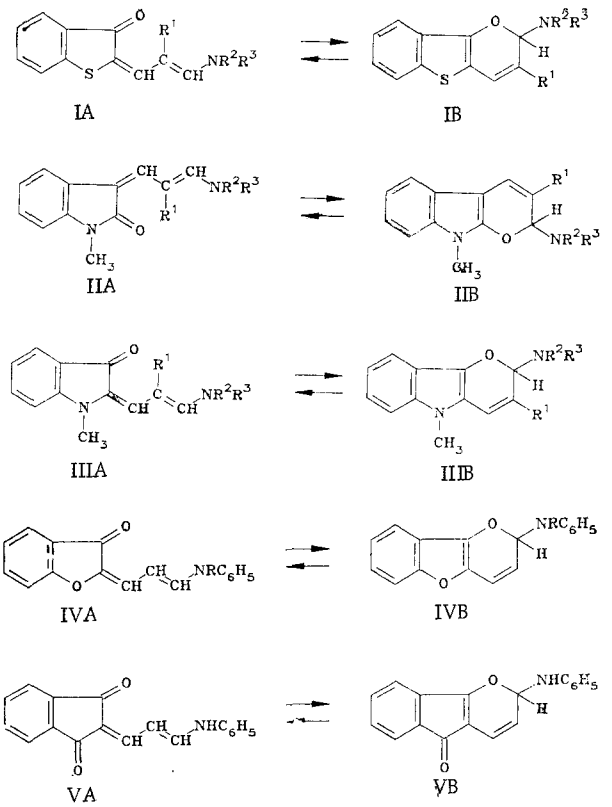
Fig. 1. Electronic spectra: a) absorption of 2-(3-phenylaminoprop-2-enylidene)benzo[b]-thiophene-3(2H)-one (Ia) in toluene (1) and in DMSO (2); 2-[3(p-methoxyphenylamino)-prop-2-enylidene]benzo[b]thiophene-3(2H)-one (Ib) in toluene (3); 2-(3-dimethylamino-prop-2-enylidene)benzo[b]thiophene-3(2H)-one (Ia) in hexane (4); b) absorption of (Ia) in isopentane—propan-2-ol (4:1) at 20 °C (1) and −80°C (2); fluorescence of (Ia) at −80°C (3).

Compounds (I-V) were synthesized by condensing the corresponding oxo derivatives with the hydrochlorides of the dianils of malon- and methylmalondialdehydes, with α-nitro-β-phenylaminoacrolein, and with acetal-aminals of β-dimethylamino- and α-methyl(phenyl)-β-dimethylaminoacrolein.

Using the methods of UV, IR, and PMR spectroscopy, it was established for compounds (I-V) containing no substituents in the propenylidene chain (R^1 = H) that the tautomeric equilibrium was shifted completely in the direction of the aminodienone form A.

The IR spectra of these compounds showed intense bands of a ring carbonyl group in the 1645-1660 cm^{-1} region and the vibrations of conjugated C=C bonds at 1590-1600 cm^{-1} (Table 1).

The electronic absorption spectra of compounds (I-V; R^1 = H) were practically insensitive to a change in the polarity of the solvent and to a variation in the substituents in the amino groups (Table 1 and Fig. 1a). Intense absorption bands in the 490-520 nm (I, III-V) and 450 nm (II) regions were shifted bathochromically by 50-70 nm relative to the long-



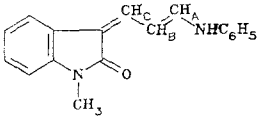
I a $R^1=R^2=H$, $R^3=C_6H_5$; b $R^1=R^2=H$, $R^3=C_6H_4OCH_3$-*p*; c $R^1=R^2=H$, $R^3=C_6H_4NO_2$-*p*; d $R^1=H$, $R^2=CH_3CO$, $R^3=C_6H_5$; e $R^1=H$, $R^2=R^3=CH_3$; f $R^1=CH_3$, $R^2=H$, $R^3=C_6H_5$; g $R^1=CH_3$, $R^2=H$, $R^3=C_6H_4NO_2$-*p*; h $R^1=R^2=R^3=CH_3$; i $R^1=C_6H_5$, $R^2=R^3=CH_3$; II a $R^1=R^2=H$, $R^3=C_6H_5$; b $R^1=R^2=H$, $R^3=C_6H_4NO_2$-*p*; j $R^1=NO_2$, $R^2=H$, $R^3=C_6H_5$; II a $R^1=R^2=H$, $R^3=C_6H_5$; b $R^1=R^2=H$, $R^3=C_6H_4NO_2$-*p*; c $R^1=H$, $R^2=CH_3CO$, $R^3=C_6H_5$; d $R^1=H$, $R^2=R^3=CH_3$; e $R^1=CH_3$, $R^2=H$, $R^3=C_6H_5$; f $R^1=CH_3$, $R^2=H$, $R^3=C_6H_4OCH_3$-*p*; g $R^1=CH_3$, $R^2=H$, $R^3=C_6H_4NO_2$-*p*; h $R^1=R^2=R^3=CH_3$; i $R^1=C_6H_5$, $R^2=R^3=CH_3$; III a $R^1=R^2=H$, $R^3=C_6H_5$; b $R^1=R^2=R^3=CH_3$; IVa R=H; b $R=CH_3CO$

TABLE 1. Spectral Characteristics of Compounds (I-V)

Compound	Solvent	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	Form	ν, cm^{-1} (in paraffin oil)
Ia	Toluene	365 (10,8), 488 (30,1)	A	1590, 1625, 1650
	DMSO	380 (11,3), 520 (45,8)	A	
Ib	Toluene	369 (8,9), 498 (28,4)	A	1590, 1620, 1645
	DMSO	375 (9,3), 524 (42,1)	A	
Ic	DMSO	384 (10,2), 512 (48,3)	A	1595, 1635, 1655
If	DMSO	354 (15,0), 503 (52,6)	A	1600, 1620, 1650
Ie	Hexane	278 (29,0), 343 (41,1), 480 (16,3)	A : B (30 : 70)	1590, 1620
	DMSO	359 (15,8), 513 (53,1)	A	
Ii	Hexane	281 (16,7), 356 (27,9), 476 (30,6)	A : B (60 : 40)	1600, 1625
	DMSO	364 (14,7), 509 (50,9)	A	
IIa	Toluene	423 (26,2)	A	1590, 1635, 1675
	DMSO	443 (39,7)	A	
IIb	DMSO	450 (37,8)	A	1600, 1635, 1680
IIh	Hexane	368 (28,1), 420 (30,4)	A : B (75 : 25)	1585, 1625, 1680
	DMSO	431 (41,3)	A	
IIIb	Hexane	326 (25,3), 368 (24,9)	B	1550, 1580
	DMSO	324 (15,5), 365 (17,1), 520 (5,4)	A : B (15 : 85)	
IVa	DMSO	353 (6,7), 482 (46,5)	A	1595, 1620, 1665
Va	DMSO	487 (35,3)	A	1585, 1630, 1650

wave absorption bands in the spectra of the anils of the corresponding heterocyclic o-hydroxyaldehydes and of 2-formylindan-1,3-dione which, according to the literature [2-5], exist in the keto-enamine forms. When the temperature was lowered, the long-wave bands in the absorption spectra of compounds (I-V; R^1 = H) contracted sharply (Fig. 1b). The observed elimination of the nonhomogeneous broadening of the band is connected with the stabilization of one of conformers of structure A in a solvent undergoing vitrification.

The aminodienone structure of the compounds mentioned was confirmed by their PMR spectra. The typical spectrum of compounds (IIa) (Fig. 2) contained the doublet of the proton of the NH group (10.5 ppm), which disappeared on deuteration. At the same time, the H_α signal (8.1 ppm) underwent a rearrangement. The triplet H_b signal at 6.4 ppm disappeared when the proton was replaced by a methyl group in the spectrum of compound (IIe).



IIa

In solutions of compounds (I; R^1 = H) in vitrifying solvents, fluorescence was observed in the 500-520 nm region with a very small Stokes shift that was excited in the absorption bands of the aminodienone form A.

Irradiation at the maximum of the long-wave band led to the isomerization of structure A of compounds (I-V) relative to the C=C bonds not accompanied by subsequent cyclization. The isomers of compounds (II) formed were stable at room temperature and were characterized by an absorption band in the 480-nm region. In hexane with irradiation by DRSh-250 lamp with a filter isolating the 436-nm line, isomerization took place completely in 15 sec; the period of half-conversion of this isomer in the initial structure was 270 sec.

For compounds (I, IV, and V) isomerization was recorded under the conditions of pulsed irradiation or on steady irradiation in a vitrifying solvent at −95°C.

The introduction of substituents into the β positions of the dienone chains of compounds (I-III; R^1 = CH_3, C_6H_5, NO_2) facilitated cyclization [1, 9]. However, in the phenylamino derivatives with R^1 = CH_3 there was no tautomerism, probably because of an increase in the efficacy of conjugation, displacing the equilibrium in the direction of the open form A.

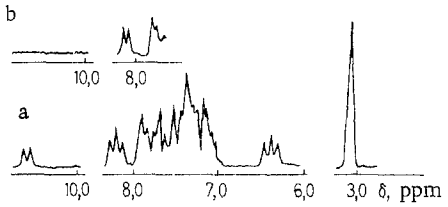


Fig. 2

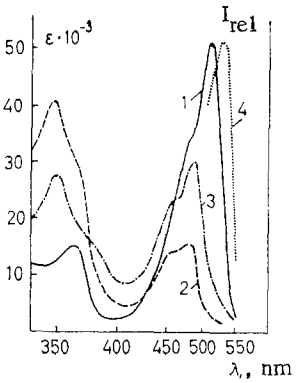


Fig. 3

Fig. 2. PMR spectrum of 1-methyl-3-(3-phenylaminoprop-2-enylidene) oxindole (IIa): a) in DMSO-D_6; b) deuteration in DMSO.

Fig. 3. Electronic spectra: absorption of 2-(3-dimethylamino-2-methylprop-2-enylidene) benzo[b]thiophene-3(2H)-one (Ih) in DMSO (1) and in hexane (2); of 2-(3-dimethylamino-2-phenylprop-2-enylidene) benzo[b]thiophene-3(2H)-one (Ii) in hexane (3); fluorescence of (Ih) in DMSO at 77°K (4).

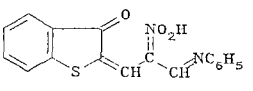
TABLE 2. Calculation of the Heats of Atomization Taking Differences in the Solvation Energies of Tautomers A and B into Account

Compound	$\Delta\Delta H_a$, kcal/mole		
	gas	ε=2,2	ε=25
Ia	22,0	7,9	−4,9
Ie	21,1	7,4	−5,1
Ij	27,7	12,2	−3,4
IIa	18,4	6,1	−6,6
IVa	20,3	7,5	−4,1

The position of the equilibrium between the aminodienone and the 2H-chromene structures in solutions of compounds (I-III) depended on the nature of the substituents in the β position of the cyclizing chain, the nature of the heterocycle, the temperature, and the polarity of the solvent. In polar solvents the equilibrium was displaced completely in the direction of form A (Fig. 3). The excitation of luminescence in the 500- and 360-nm regions caused a single fluorescence band (λ_{max} 540 nm) corresponding to the noncyclic form. On passing to solvents with higher dielectric constants, the amount of the 2H-chromene tautomer B rose in the sequence of substituents R^1 = H < C_6H_5 < CH_3 in accordance with their steric constants. In the absorption spectra under the same conditions a band at 350 nm that is characteristic for the cyclic form [6] appeared, overlapping with the aminodienone absorption band at 360 nm (Table 1).

The complete displacement of the equilibrium in the direction of cyclic structure B was observed for 2-(γ-dimethylamino-β-methylprop-2-enylidene)-1-methylindoxyl (IIIb). The ratios of the tautomers A and B in the equilibrium mixtures, determined from the magnitude of the extinction coefficient of the long-wave maximum, are shown in Table 1.

In the luminescence spectra of frozen solutions of the tautomeric compounds in isopentane at 77°K, two fluorescence bands corresponding to the aminodienone and cyclic structures



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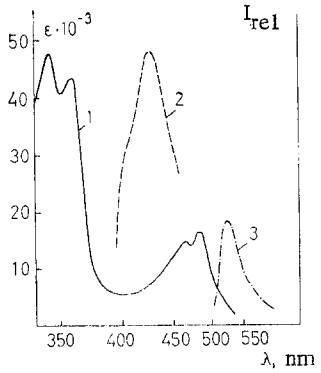

Fig. 4

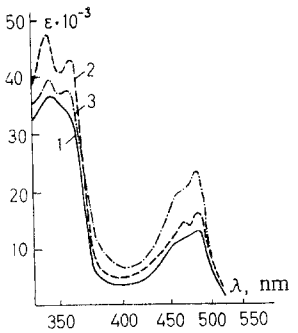

Fig. 5

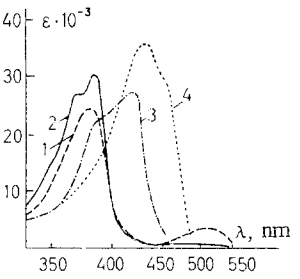

Fig. 6

Fig. 4. Electronic spectra of (Ih) in isopentane: absorption (1); fluorescence at 77°K, λ_{exc} = 340 nm (2); λ_{exc} = 480 nm (3).

Fig. 5. Electronic absorption spectra of (Ih) in isopentane: at 20°C (1) and at −95°C (2); after irradiation at −95°C with λ_{max} = 365 nm for 1200 sec (3).

Fig. 6. Electronic absorption spectra in isopentane: 2-(3-dimethyl-amino-2-methylprop-2-enylidene)-1-methylindoxyl (IIIb) at 20°C (1) and at −95°C (2); 3-(3-dimethylamino-2-methylprop-2-enylidene)-1-methyl oxindole (IIh) at 20°C (3) and −95°C (4).

were recorded (Fig. 4). Their assignment was made on the basis of the fluorescence excitation spectra. In compound (Ij) in polar solvents, the tautomeric equilibrium had a more complex nature, C ⇄ A ⇄ B, probably because of the appearance of the aci form (Ic).

The aci form absorbed at 560 nm and, in contrast to structures A and B, did not exhibit luminescence.

The thermochromic properties of compounds (I-III; R^1 = CH_3, C_6H_5) also depended on the nature of the heterocycle. Lowering the temperature of a solution of (Ih) in a vitrifying solvent to −95°C did not affect the position of the equilibrium A ⇄ B. However, irradiation at the absorption maximum of the 2H-chromene form caused the ring to open and displaced the equilibrium in the direction of the aminodienone form A (Fig. 5). Raising the temperature to 20°C restored the initial equilibrium, which corresponds to the thermochromic transformation $B \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} A$.

In a solution of compounds (IIIb), when the temperature was lowered to −95°C, the equilibrium shifted in the direction of the 2H-chromene form, and in a solution of (IIh) in the direction of the aminodienone form (Fig. 6). The equilibrium shifted in the same direction on prolonged irradiation at the absorption maximum of the cyclic structure.

The conclusions drawn on the basis of the electronic absorption and emission spectra were confirmed by the PMR spectra of compounds (I-III). Thus, while in a solution of (Ih) in a polar solvent (DMSO-D_6) the signals of the protons of the $N(CH_3)_2$ and C—CH_3 groups, corresponding to the aminodienone form A, appeared at 3.10 and 2.15 ppm, in carbon disulfide, in addition to these, there were signals of the protons of these groups in the cyclic form B displaced upfield to 2.30 and 1.90 ppm, respectively.

The amount of the 2H-chromene tautomer in carbon disulfide calculated from the integral intensities of these signals was 65%, which was close to its proportion in hexane.

The results obtained are in harmony with those of quantum-chemical calculations of the relative stabilities of tautomers A and B performed by the SFC MO PPP method in the σ,π-parametrization of Dewar taking the influence of the solvent into account (Table 2).

EXPERIMENTAL

The electronic absorption spectra were measured on a Specord UV-vis spectrometer with an attachment for a smooth change in the temperature of the sample, and the luminescence

TABLE 3. Characteristics of Compounds (I-V)

Compound	mp, °C	Found, %			Empirical formula	Calculated, %		
		C	H	S		C	H	S
Ib	239	69,6	4,8	10,1	$C_{18}H_{15}NO_2S$	69,9	4,9	10,4
Ic	298	62,9	3,8	10,0	$C_{17}H_{12}N_2O_3S$	63,0	3,7	9,9
Id	233	69,9	4,8	9,9	$C_{19}H_{15}NO_2S$	71,0	4,7	10,0
Ie	182	67,7	5,8	13,9	$C_{13}H_{13}NOS$	67,5	5,7	13,9
If	268	73,6	5,3	10,8	$C_{18}H_{15}NOS$	73,7	5,2	10,9
Ig	312	64,2	4,4	9,4	$C_{18}H_{14}N_2O_3S$	63,9	4,2	9,5
Ih	190	68,2	6,0	13,4	$C_{14}H_{15}NOS$	68,5	6,2	13,1
Ii	212	74,5	5,8	10,2	$C_{19}H_{17}NOS$	74,2	5,6	10,4
Ij	144	63,3	3,9	9,6	$C_{17}H_{12}N_2O_3S$	62,9	3,7	9,9
IIa	219	78,1	6,0		$C_{18}H_{16}N_2O$	78,2	5,8	
IIb	318	67,0	4,9		$C_{18}H_{15}N_3O_3$	67,3	4,7	
IIc	192	75,2	5,9		$C_{20}H_{18}N_2O_2$	75,5	5,7	
IId	155	73,5	7,0		$C_{14}H_{16}N_2O$	73,7	7,1	
IIe	211	78,3	6,3		$C_{19}H_{18}N_2O$	78,6	6,2	
IIf	147	74,7	6,2		$C_{20}H_{20}N_2O_2$	75,0	6,3	
IIg	320	71,3	5,3		$C_{19}H_{17}N_3O_2$	71,4	5,4	
IIh	163	74,4	7,6		$C_{15}H_{18}N_2O$	74,4	7,5	
IIi	189	79,2	6,7		$C_{20}H_{20}N_2O$	78,9	6,6	
IIIa	216	78,0	6,0		$C_{18}H_{16}N_2O$	78,2	5,8	
IIIb	112	74,6	7,4		$C_{15}H_{18}N_2O$	74,4	7,5	
IVa	210	77,3	4,9		$C_{17}H_{13}NO_2$	77,6	5,0	
IVb	189	74,5	4,8		$C_{19}H_{15}NO_3$	74,7	4,9	
Va	283	78,7	4,7		$C_{18}H_{13}NO_2$	78,5	4,7	

spectra on a Fotolyum instrument (TsKB AMN SSSR [Central Design Bureau of the Academy of Medical Sciences of the USSR]). IR absorption spectra were taken on a UR-20 spectrometer, and PMR spectra on a Varian XL-100/15 spectrometer at concentrations of 3-5% with HMDS as internal standard. The method of calculating the relative stabilities of tautomers A and B by the SFC MO PPP method in the σ,π-parametrization of Dewar taking the influence of the solvent into account has been described previously [7].

The hydrochlorides of the dianils of malon- and methylmalondialdehydes were obtained by a similar procedure to that of Klimko and Skoldinov [8] $p\text{-}XC_6H_4N{=}CHC(R){=}CHNHC_6H_4X\text{-}p\cdot HCl$ (R = H, X = CH_3O, mp 236°; R = H, X = NO_2, mp 264°; R = CH_3, X = CH_3O, mp 249°; R = CH_3, X = NO_2, mp 270°). The acetal-aminals of β-dimethylamino- and α-methyl(phenyl)-β-dimethylaminoacroleins were synthesized as described in [9, 10].

The γ-Arylaminoprop-2-enylidene Derivatives (Ia-c, g), (IIa, b, e-g), (IIIa), (IVa), and (Va). Ethanolic solutions of equimolar amounts of 3-hydroxybenzo[b]thiophene, 1-methyloxindole, 1-methylindoxyl (in an atmosphere of argon), 3-hydroxybenzo[b]furan, or indan-1,3-dione were added with stirring in the presence of sodium acetate to suspensions of the hydrochlorides of the dianils of malon- and methylmalondialdehydes in absolute propan-2-ol or butanol (Ic, g; IIb, f), and the mixtures were boiled for 0.5-2 h. The substances were purified by crystallization from propan-2-ol or DMSO—propan-2-ol. Yields 50-70%.

The γ-Dimethylaminoprop-2-enylidene Derivatives (Ie, h, i), (IId, h, i), and (IIIb). With stirring, ethereal solutions of equimolar amounts of 3-hydroxybenzo[b]thiophene, 1-methyloxindole, or 1-methylindoxyl (in an atmosphere of argon) were added to solutions of the appropriate acetal-aminals in absolute ether. The resulting precipitates were filtered off, purified by chromatography (Al_2O_3, chloroform) and crystallized from octane or propan-2-ol. Yields 50-80%.

2-(β-Nitro-γ-phenylaminoprop-2-enylidene)-benzo[b]thiophene-3(2H)-one (Ij). With stirring, a solution of 0.75 g (5 mmole) of 3-hydroxybenzo[b]thiophene in 4 ml of propan-2-ol was added to a suspension of 0.96 g (5 mmole) of α-nitro-β-phenylaminoacrolene [11] in 8 ml of absolute propan-2-ol, and the mixture was boiled for 1 h. The precipitate was purified by chromatography [Silochrome C-120; CCl_4—C_6H_6 (1:1)] and was crystallized from ethanol. Yield 46%.

The γ-(N-acetyl-N-phenylamino)prop-2-enylidene derivatives (Id), (IIc), and (IVb) were obtained by the acylation of the sodium salts of compounds (Ia), (IIa), and (IVa) by the method of Palui et al. [12] and were purified by crystallization from propan-2-ol (Id), carbon tetrachloride (IIc), and isooctane (IVb).

The melting points and elementary analyses of the compounds obtained are given in Table 3.

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CONDENSED HETEROCYCLES.

42.* SYNTHESIS AND SOME PROPERTIES OF 3-HYDROSELENOBENZO[b]FURAN-2-CARBALDEHYDE AND 2-HYDROSELENOBENZO[b]FURAN-3-CARBALDEHYDE

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The reactions of 3-chlorobenzo[b]furan-2-carbaldehyde and 2-bromobenzo[b]furan-3-carbaldehyde with sodium hydrogen selenide have yielded isomeric hydroseleno aldehydes which, under the action of atmospheric oxygen, have oxidized to diselenides, while alkylation of the seleno aldehydes with methyl iodide leads to the formation of the corresponding methylseleno derivatives.

Ortho-bifunctionally substituted heterocycles are attracting attention as intermediates in the synthesis of various condensed heterocyclic systems, and also of different substances with properties of practical use [2, 3]. Continuing the search for methods of synthesizing and of studying the structure and properties of hydroxy, mercapto, and seleno aldehydes and aldimines of the heterocyclic series, we have made an attempt to synthesize previously unknown isomeric hydroselenobenzo[b]furancarbaldehydes.

One of the possible methods of obtaining ortho-hydroseleno aldehydes of the heterocyclic series is the nucleophilic replacement of hydrogen atoms in the corresponding ortho-halo aldehydes by a hydroseleno group. Thus, isomeric hydroselenobenzo[b]thiophenecarbaldehydes have previously been synthesized by this method [4]. The initial compounds for obtaining hydroselenobenzo[b]furancarbaldehydes — 3-chlorobenzo[b]furan-2-carbaldehyde (I) and

*For communication 41, see [1].

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